

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
21 March 2002 (21.03.2002)

PCT

(10) International Publication Number  
**WO 02/23557 A1**

(51) International Patent Classification<sup>7</sup>: **H01B 12/00**

(21) International Application Number: **PCT/US01/28929**

(22) International Filing Date:  
14 September 2001 (14.09.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/232,747 15 September 2000 (15.09.2000) US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

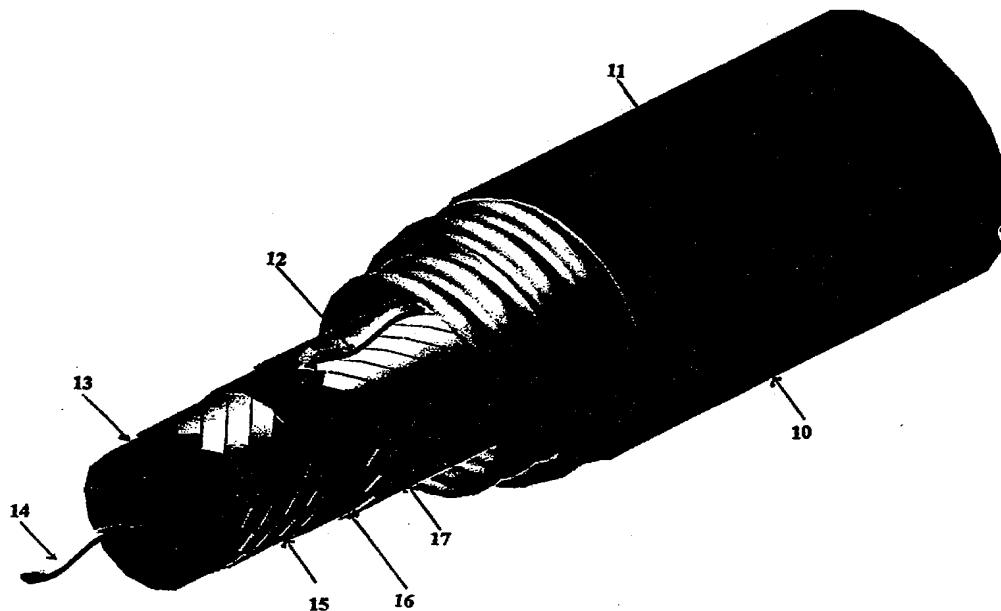
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declaration under Rule 4.17:**

— of inventorship (Rule 4.17(iv)) for US only

[Continued on next page]

(54) Title: **SUPERCONDUCTING CABLE**



(57) Abstract: Tape-shaped superconducting wires (15) include a covering of a stabilizing metal and are wound on a flexible former (13). The superconducting wires are laid on the former (13) at a bending strain of not more than 0.2%. The wires (15) are laid side-by-side to form a first layer. A prescribed number of tape-shaped superconducting wires are laid on top of the first layer side-by-side to form a second layer. The former may be made of a metal, plastic, reinforced plastic, polymer, or a composite and imparts flexibility to the cable.

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WO 02/23557 A1



**Published:**

— *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## SUPERCONDUCTING CABLE

### BACKGROUND OF THE INVENTION

#### FIELD OF THE INVENTION

The present invention relates to a superconducting cable employing a flexible oxide superconductor, and more particularly, it relates to forming a superconducting cable. This invention also relates generally to solvent welding of laminated film and to supercritical solvent welding of oriented films.

#### DESCRIPTION OF THE BACKGROUND ART

Superconducting materials are those where the electric resistance approaches zero ( $1\mu\text{v}/\text{cm}$ ) below a critical temperature, its value depending on the material. Superconductivity is defined within a critical surface, i.e. a graph or figure with its axes being temperature, electrical current and magnetic field. Thus, for a given working temperature there is a defined curve of critical current which is a function of the magnetic field generated and/or applied to the superconductor.

The best known superconductor materials are NbTi and Nb<sub>3</sub>Sn, however their working temperature is only 4.2K, the boiling temperature of liquid helium. This is the main limitation to large scale application of these superconducting materials. Such superconductors are therefore used almost exclusively for winding of magnets. Manufactured from wires (NbTi and Nb<sub>3</sub>Sn) or tapes (Nb<sub>3</sub>Sn) with high critical current densities (3500 A/mm<sup>2</sup> 5 Tesla for NbTi), such winding of compact magnets provide the production of high fields (up to 18 Tesla) in large volumes.

These superconductor magnets are used for the formation of medical images by nuclear magnetic resonance (MRI) and for materials analysis by the same principle (NMR), the magnets for ore separation and research magnets for high fields, such as those used in large particle accelerators (SSC, HERA, KEK, etc.).

Oxide superconductors of higher critical temperatures were discovered in 1986. These are intermetallic compounds involving metal oxides and rare earths, with perovskite (mica) crystal structure. Their critical temperatures vary from 30K to approaching room temperature and their critical fields are above 60 Tesla. Therefore these materials are considered promising and may replace  $\text{Nb}_3\text{Sn}$  and  $\text{NbTi}$  in the manufacture of magnets and find other applications not feasible with liquid helium, such as transmission of electricity. Such materials have not previously been available as wires, cables, films, tapes or sheets.

An oxide superconductor which enters the superconducting state at the temperature of liquid nitrogen would be advantageous for application in a superconducting cable having a cooling medium of liquid nitrogen. With such an application, it would be possible to simultaneously attain simplification of the thermal protection system and reduction of the cooling cost in relation to a superconducting cable which requires liquid helium.

A superconducting cable must be capable of transmitting high current with low energy loss in a compact conductor. Power transmission is generally made through an alternating current, and a superconductor employed under an alternating current would inevitably be accompanied by energy loss, generically called AC loss. AC losses such as hysteresis loss, coupling loss, or eddy current loss depends on the critical current density of the superconductor, size of filaments, the structure of the conductor, and the like.

Various types of superconducting cables have been experimentally produced using metallic superconductors to study the structures for reducing AC loss, such as a superconductor which comprises a normal conductor and composite multifilamentary superconductors which are spirally wound along the outer periphery of the normal conductor. The conductor is formed by clockwise and counterclockwise wound layers of composite multifilamentary superconductors, which are alternately superimposed with each other. The directions for winding the conductors are varied every layer for reducing magnetic fields generated in the conductors, thereby reducing impedance and increasing current carrying capacity thereof. This conductor has a high-resistance or insulating layer between the layers.

When a cable conductor is formed using an oxide superconductor, the technique employed in a metal superconductor cannot be used. An oxide superconductor, i.e., a ceramic superconductor, is fragile and weak in mechanical strain compared with a metal superconductor. For example, the prior art discloses a technique of spirally winding superconductors around a normal conductor so that the winding pitch is equal to the diameter of each superconductor. However, when a superconducting wire comprising an oxide superconductor covered with a silver sheath is wound at such a short pitch, there is a high probability that the oxide superconductor will be broken, thereby interrupting the current. When an oxide superconducting wire is extremely bent, its critical current may also be greatly reduced.

The cable conductor must be flexible to some extent to facilitate handling. It is also difficult to manufacture a flexible cable conductor from a hard, fragile oxide superconductor.

Polyolefins are the most widely used class of polymers in the world today. They have been made popular by both their useful physical and mechanical properties as well as their inexpensive manufacturability. Because of the inexpensive nature of these polyolefins many attempts have been made to increase the physical and mechanical properties so as to further extend the scope of applications of these polymers. Perhaps the most widely practiced technique for this purpose is orientation. It is well known that upon drawing, the modulus, ultimate strength, tear resistance and puncture resistance are all increased in the draw direction, Ajji, A.; Legros, N.; Dumoulin, M.M. *Advanced Performance Materials* 1998, 5, 117-136. Unfortunately, all of these properties are simultaneously reduced in the transverse direction. Biaxial orientation has led to some degree of success, however the increased material properties are not as significant. It is therefore clear that in order to fully exploit the benefits of orientation, one must find a way to suppress the undesirable decrease in material properties in the transverse direction. One way to accomplish this is to create a quasi-isotropic composite of oriented polyolefins. It would also be beneficial if this could be done without the addition of an adhesive, which itself will serve to change the material properties of the system.

Welding of polymers has received much attention in the polymer community over the last 30 years. The goal of any polymer welding technique is to produce a bond between two polymers (alike or dislike), such that after welding, the weld interface is free of defects and has high structural integrity. Ideally the welded joint will have mechanical and physical properties approaching that of the bulk

polymer. Researchers have developed many methods to weld polymers, all of which have experienced varying degrees of success in practical use.

Perhaps the oldest and most effective procedure for welding polymers involves melt pressing. In this procedure, two polymer substrates are first taken above the melt temperature for semi-crystalline polymers, or above the softening temperature for amorphous polymers. The substrates are then placed in contact with some initial normal force to produce intimate contact and allowed to interdiffuse. In many cases it is possible to produce a welded joint with good mechanical and physical properties. In general, this technique is simple and it is by far the most widely used and effective. Many researchers have extended this simple idea to more elaborate schemes. R. S. Porter and W. T. Mead, Mead, W.T.; Porter, R.S.J. *Appl Polym Sci* 1978, 22, 3249-3265, have taken this simple concept and created single polymer composites, (composites which are composed of a single type of polymer). By exploiting the difference in melting temperature between High Density Polyethylene (HDPE) fibers (ca. 139°C) and conventional HDPE (ca. 132°C) or Low Density Polyethylene (LDPE) (ca. 110°C), Porter et. al. were able to embed the HDPE fibers into either a HDPE or LDPE matrix, with only minimal relaxation of the fibers. Due to the extremely high degree of orientation in the fibers, they retained a great deal of strength even after relaxation. Similarly, V. Thomas and J. T. Tielking, Thomas, V.; Tielking, J.T.; Wolfenden, A.; Said, M.A. *Annu Tech Conf ANTEC Conf Proc* 1996, 3, 3234-3238; and Thomas, V.; Said, M.A. *Annu Tech Conf ANTEC Conf Proc* 1997, 2, 2362-2366, created non-woven fabrics by extruding polymer filaments directly onto a thin polymer film carrier. In both instances the adhesion is due to polymer interdiffusion while in the melt as well as epitaxial transcrystallization. Although this is a very useful and flexible technique, it is always necessary to melt or soften the polymers to the point of flow. Hence, it is normally very difficult to retain any morphology, i.e. crystallinity and orientation, that is in the polymer substrate prior to welding.

Ultrasonic welding is a technique that employs high frequency (10-40 kHz) low amplitude (1-25  $\mu\text{m}$ ) mechanical vibrations to induce cyclical deformation in the polymers. This deformation causes intermolecular friction that converts the mechanical energy to heat. When enough energy has been supplied to overcome the softening temperature, the parts interdiffuse and a weld is achieved, Lin, S.J.; Lin, W.F.; Chang, B.C.; Wu, G.M.; Hung, S.W. *Adv Polym Technol* 1999, 18, 125-135. Ultrasonic welding is an important process in industry because it is fast and economical. However,

it is best suited to polymers with low softening temperatures and is difficult to adapt to crystalline polymers or polymers with low stiffness. Ultrasonic welding also ultimately relies on thermally induced flow, which means it suffers from most of the drawbacks of conventional melt pressing. Another technique which is widely used for the bonding of polymers is solvent welding. With this technique a solvent or softening agent is applied to the surface of the polymers, and the two surfaces are brought together with an applied force. The adhesion, in this case, is due to diffusion of the solvated/softened material at the interface of the two polymers. C. Y. Yue et. al., Yue, C.Y.; Cherry, B.W. *Adhesion* (Barking, England) 1986, 147-177, reviewed the structure and strength of solvent welded joints. Yue notes that even after elaborate drying procedures and very long drying times (days to weeks) some solvent always remains in the polymer. This solvent remains in the vicinity of the bond and has a deleterious effect on the strength of the material at that point. Yue found that the bond strength was directly related to the size of this solvent affected region. More recently F. Beaume and N. Brown, Beaume, F.; Brown, N. *Journal of Adhesion* 1993, 43, 91-100, have studied the solvent welding of polyamide - 11. They too found that the strength of the bond was effected by this solvent affected region, and that since the solvent could never be fully removed, initial material strength could not be attained. In addition to the mechanical effects of this residual solvent, it should also be noted that this technique often employs halogenated solvents, which are highly regulated and must be treated as hazardous waste. This leads to the solvent welded polymers themselves often being treated as hazardous waste due to the residual solvent. Most solvent welding has traditionally been restricted to amorphous polymers, and has found little or no use with crystalline or semi-crystalline polymers.

In recent years, supercritical carbon dioxide (SC CO<sub>2</sub>) has received much attention in the polymer community due to its unique solvent properties. The scope of the field is described in a recent review paper by Andrew I. Cooper, Cooper, A.I. *Journal of Materials Chemistry* 2000, 10, 207-234. Although supercritical CO<sub>2</sub> is a non-solvent for most polymers, it plasticizes most polymers very efficiently. McCarthy et. al., Kung, E.; Lesser, A.J.; McCarthy, T.J. *Macromolecules* 1998, 31, 4160-4169, have shown that the increased free volume in the swollen polymers is actually sufficient to allow chemical reactions within the bulk of a polymer. This increase in free volume leads to a decrease in viscosity and hence an increase in chain mobility. Lesser et. al., Hobbs, T.; Lesser, A.J.; *J Polym Sci Part B* 1999, 37, 1881-1891, have exploited this effect in the drawing of fibers, attaining higher draw ratios than are attainable under ambient conditions. It is important to note that the

carbon dioxide permeates the amorphous regions only, leaving the crystal structure undisturbed, thus allowing semi-crystalline polymers to retain their integrity during and after the process. Because the CO<sub>2</sub> reverts to a gas under ambient conditions, this solvent is easily and completely removed after treatment. This allows SC CO<sub>2</sub> to act as a reversible plasticizing agent.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide a superconducting cable having flexibility and exhibiting excellent superconductivity, particularly high critical current and high critical current density, having an oxide superconductor.

Another object of the present invention is to provide such a superconducting cable which is reduced in AC loss.

According to the present invention a superconducting cable is provided employing an oxide superconductor, which comprises a flexible core member, and a plurality of tape-shaped oxide superconducting wires which are wound on the core member, without an electric insulating layer between the superconducting wires or between the core member and the superconducting wires. In the inventive conductor, each of the oxide superconducting wires consists essentially of an oxide superconductor and a stabilizing metal covering the same. The plurality of tape-shaped superconducting wires laid on the core member form a plurality of layers, each of which is formed by laying a plurality of tape-shaped superconducting wires in a side-by-side manner. The plurality of layers are successively stacked on the core member. This core member provides the inventive superconducting cable with flexibility. The superconducting cable according to the present invention maintains a superconducting state at the temperature of liquid nitrogen.

The conductor according to the present invention further provides an AC conductor which is reduced in AC loss.



The present invention also includes a novel approach to solvent-welding semi-crystalline polymers wherein supercritical carbon dioxide is used as the plasticizing agent. This process is used to fabricate quasi-isotropic laminated films from highly oriented LLDPE film. The interfacial adhesion between individual plies of the laminate is increased over prior art processes without detriment to other physical and mechanical properties of the laminate.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view showing the multilayer structure of the present invention;

FIG. 2 is a sectional side view showing one embodiment of the present invention;

FIG. 3 is a sectional side view showing another embodiment of the present invention;

FIG. 4 is a depiction of the embossing pattern used in the present invention.

FIG. 5 is a schematic drawing of the Supercritical CO<sub>2</sub> processing chamber. The chamber allows for the application of a normal force to the substrate while in the presence of CO<sub>2</sub>.

FIG. 6 is a Differential Scanning Calorimetry (DSC) for the LLDPE films.

FIG. 7 is a Wide Angle X-Ray Scattering (WAXS) of an 8-layer laminated film showing the 8-fold symmetry indicative of the retention of orientation in each ply.

FIG. 8a depicts the results of tensile tests on (————) 8-layer laminated films with a draw ratio of 2 as compared to its single ply constituents tested both with the (— ■ —) draw direction and in the (— ■ — ■ —) transverse direction.

FIG. 8b depicts the results of tensile tests on (■ ■ ■ ■) 8-layer laminated films with a draw ratio of 5 as compared to its single ply constituents tested in the (————) draw direction.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to a high temperature superconductor cable which may be used in the shielded or unshielded form of construction. There are many applications where both shielded and unshielded cables serve useful purposes.

A modification of this embodiment is to insulate the cable with dielectrics over the high temperature superconductor tapes and then provide another high temperature superconductor layer over the dielectric. The entire cable is then either introduced into a cryostat of the type described above or a cryostat is constructed over the cable. This coaxial construction forces the magnetic field to stay between the inner and the outer layers of high temperature superconductor tapes. There is substantially no magnetic field outside the high temperature superconductor tapes and therefore there is no eddy current in the outer metallic enclosures. With this construction very large amounts of current can be carried depending upon the number of tapes present in the cable. The limitation in this cable design is that the dielectric remains at the cryogenic temperature and a material which can withstand the cryogenic temperature without any physical and mechanical degradation has to be used. The polymeric dielectric material of one embodiment of the present invention has good physical and mechanical properties at liquid nitrogen and lower temperatures. It has high dielectric strength and high breakdown voltage.

Advantageously the cable of the present invention includes the use of a flexible stainless steel corrugated pipe, which is optionally covered with a wire braid or mesh. Preferably, the corrugated pipe is drilled with holes of a size and pattern to allow the liquid nitrogen to flow into the butt gaps of the high temperature superconductor tapes and flood the dielectric material. The high temperature superconductor tapes are laid in a special manner to simulate two layer construction allowing maximum current to flow through the cable.

The dielectric material advantageously consists of semi-conductive tape, aluminized shield tape, and polymeric dielectric tapes. A typical construction of a shielded cable is shown in Fig. 3. An unshielded cable can be constructed by omitting the outer layers of high temperature superconductor tapes. This cable construction is shown in Fig. 2. The present invention includes both shielded and

unshielded high temperature superconductor cable. The design differs from other known cables in the case of an unshielded cable where an extrusion of dielectric material is performed over the thermal insulation cryostat. The prior art does not disclose any method of construction for shielded high temperature superconductor cable.

Referring to Fig. 1, superconductor cable 10 is shown having flexible, evacuated double walled, outer pipe 11, through which liquid nitrogen, 12, flows to a chiller. Ground-potential superconductive shield material 17 encircles dielectric and shield layer 16, which in turn surrounds current carrying superconductive material 15. The flexible, porous-walled inner pipe, 13, is encircled by superconducting material 15 and provides a central, tube-like portion for transport of liquid nitrogen from the chiller. In one embodiment pipe 13 further has a braided surface that contacts superconductive material 15.

Fig. 2 illustrates an embodiment of an unshielded cable wherein former 21 is surrounded by semiconductive bedding tape 22, upon which is laid superconductive tape 23. Another layer of semiconductive bedding tape 24 surround superconductor tape 23. Shielding layer 25 encircles bedding tape 24 and dielectric layer 26 surrounds shielding layer 25. Dielectric layer 26 is encircled by shield layer 27 which in turn is encircled by semiconductive bedding layer 28. Bedding layer 28 is surrounded by binder tape 29, which is encompassed by centering ring 30, in turn surrounded by jacketed cryostat 31.

Referring to Fig. 3, which shows an embodiment of a shielded cable, jacketed cryostat 53 encompasses centering ring 52, which surrounds binder tape 51, which in turn encircles semiconductive tape 50. Tape 50 encircles superconductive tape 49, which surround semiconductive bedding tape 48, which encompass shielding layer 47. Dielectric 46 encircles shield layer 45, which surrounds semiconductive tape 44. Superconductive tape 43 encircles semiconductive bedding tape 42, which surrounds former 41.

The present invention relates to a cable employing an oxide superconductor comprising a flexible core member, a plurality of tape-shaped oxide superconducting wires laid on said core member with tension of not more than about 2 kgf/mm<sup>2</sup> and a bending strain of not more than about 0.2% on the superconductor, wherein each tape-shaped superconducting wire consists essentially of an oxide

superconductor and a stabilizing metal covering the same, said plurality of tape-shaped superconducting wires forming a plurality of layers each being formed by laying said tape-shaped superconducting wires in a side-by-side manner, said plurality of layers being successively stacked on said core member without an insulating layer between the plurality of layers and the core member, said core member providing said superconducting cable with flexibility, said superconducting cable capable of maintaining a superconducting state at the temperature of liquid nitrogen, said wires having substantially homogeneous superconducting phases along the longitudinal direction of said wire, the c-axes of said superconducting phases being oriented substantially in parallel with the direction of thickness of said wire, said superconducting wires being formed by grains aligned in parallel extending along the longitudinal direction of said wire, said grains being stacked along the direction of thickness of said wire.

The superconducting cable advantageously has flexibility such that its superconductivity does not substantially deteriorate upon bending up to about 50 times the diameter of the cable. It is also advantageous that the core member be selected from the group consisting essentially of metals, plastics, reinforced plastics, polymers, and composites. One embodiment of the superconducting cable provides a core member being a pipe having a spiral groove surface, a web shaped surface, a mat shaped surface, or a braid shaped surface on its exterior which forms a surface for the tape-shaped superconducting wires. The inventive superconducting cable does not have any insulating layer between the plurality of layers of the tape-shaped superconducting wires. Advantageously the tape-shaped wires are laid on said core member with the tape-shaped plurality of layers being laid on the surfaces formed by said immediately prior layer of tape-shaped wires. In another embodiment the wires are twisted within said tape-shaped stabilizing metal covering. Advantageously in the superconducting cable said tape-shaped wires are laid at a lay angle of up to about 90 degrees, advantageously from about 10 to about 60 degrees, and preferably from about 20 to about 40 degrees. One embodiment of the present invention includes a superconducting cable having at least two distinct groups of tape-shaped wire layers. Advantageously the lay angle of each successive layer of tape-shaped wires alternate in lay direction or pitch; and each said successive layer consists of at least two tape-shaped wires. Advantageously, a layer of dielectric material separates each of the at least two distinct groups of tape-shaped wire layers. Preferably, a layer of dielectric material separates the core member from the layer of tape-shaped wires closest thereto. Advantageously, the dielectric material is selected from the group consisting of polypropylene, polyethylene, and

polybutylene. In one embodiment of the present invention the at least two distinct groups of tape-shaped wire layers carries approximately equal amounts of the current flowing through the cable. Also advantageous is where the group of tape-shaped wire layers furthest from the core member provides shielding of the current flowing through the other layers and reduces magnetic fields or eddy currents in the cable. Preferably, the stabilizing metal used in the present invention is selected from the group consisting of silver, silver alloys, and nickel and nickel alloys, which may require a buffer layer.

Included in the present invention is an embodiment in which each tape-shaped multifilamentary oxide superconducting wire has such a structure that is a number of filaments consisting essentially of an oxide superconductor contained in a stabilizing material of silver, silver alloys, nickel and nickel alloys. The oxide superconductor may be prepared from an oxide superconductor such as bismuth, strontium, calcium and copper oxide.

Advantageously, each of said plurality of layers contains at least 2 tape-shaped silver contained wires per layer. Preferably, each of said plurality of layers contains at least 4 tape-shaped wires per layer. One embodiment of the present invention includes an insulating layer between the second and third layer of said plurality of layers. Where there are more than 4 layers, advantageously, an insulating layer is present between each second and third layer of said plurality of layers.

In the inventive conductor, the core member, which is generally called a former, is adapted to hold the tape-shaped superconducting wires at a bending strain of the prescribed range. This former has a length which is required for the superconducting cable conductor, and is provided at the center of the superconducting cable conductor. The former is in a substantially cylindrical or spiral shape so that the tape wires are laid thereon, and generally has a substantially constant diameter along its overall length. The former can consist essentially of at least one material selected from the group consisting of metals such as stainless steel, copper, aluminum and the like and plastics, reinforced plastics and ceramics.

According to the present invention, the former is preferably in the form of a tubular member having flexibility. It is also possible to employ a pipe having a spiral groove (hereinafter referred to as a spiral tube) as a former having sufficient strength and flexibility. A bellows tube having a bellows

may also be employed as a former. Further, the former can also be prepared from a spirally wound material such as a spiral steel strip. Each of these shapes is adapted to provide the former with sufficient flexibility. The flexible former provides the inventive conductor with flexibility. The flexible conductor of the present invention can be taken up on a drum.

When practicing the present invention, it is possible to lay or wind several tape-shaped multifilamentary superconducting wires on the former. The tape wires may be laid in two or more layers while directing a surface thereof to the former. Each layer may be formed by an arbitrary number of the tape wires. When several tape wires are laid on the former in parallel with each other so that the surface of the former is filled up with the tape wires, additional tape wires are further wound thereon. When a sufficient number of tape wires are wound on the first layer of the tape wires as a second layer, a third layer of tape wires are then wound thereon. No insulating layer is provided between each adjacent pair of layers.

In the present inventive method, each tape-shaped multifilamentary oxide superconducting wire is laid or wound on a former having a prescribed diameter at a bending strain or a curvature of a prescribed range and a pitch of a prescribed range. A relatively loose bending is applied to the tape wire along its longitudinal direction. The tape wire which is wound on the former is bent at a bending strain of not more than 0.4%, preferably not more than 0.3%. Superconductivity of the tape wire is not substantially reduced upon bending at a bending strain of such a range, as compared with that in a linear state.

The present invention it is preferable to adjust the pitch and the diameter of the former so that the bending strain of the superconductive wire is not more than 0.2%. Each tape-shaped multifilamentary oxide superconducting wire is preferably wound on the former with tension of not more than  $2 \text{ kgf/mm}^2$  in a range of 0.5 to  $2 \text{ kgf/mm}^2$ .

The core member (former) can be formed by either an electric insulating material or an electric conductor. The electric insulating material is preferable in consideration of reduction in AC loss, while a metal which is a conductor is preferable in consideration of strength. A metal pipe having a spiral groove or a metal bellows tube may be used as the core member for providing the conductor with flexibility while maintaining constant strength. A metal core member can also be employed for

safety in the case of an accidental abnormal current. In this case, it is possible to set optimum resistivity of the core member in consideration of AC loss of the conductor and the core member for the abnormal current.

When a metal pipe, which optionally may have a spiral groove, or a metal bellows tube is employed as the core member, the conductor can further comprise a metal tape which is laid or wound on the core member, and dielectric tape which is laid on a the outside surface of the metal tape. The metal tape can form a smooth surface for covering any grooves of the core member so that the superconducting tapes do not buckle. It is possible to cover any grooves while maintaining flexibility of the core member by laying the metal tape.

According to the present invention, it is possible to employ tape-shaped multifilamentary wires each having twisted filaments. The filaments forming a superconducting multifilamentary tape are twisted at a prescribed pitch. Due to such twisting of the filaments, an induction current flowing between a stabilizing metal and the filaments is parted every twisting pitch into small loops, and hence the value of the current is limited. Thus, generation of Joule heat is suppressed in the stabilizing metal and AC loss is reduced as compared with a superconducting wire having untwisted filaments.

The superconducting cable conductor according to the present invention has such flexibility that its superconductivity is substantially not deteriorated also when the same is bent up to 50 times the diameter of the cable. This conductor can be wound on a drum, to be stored and/or transported.

The present invention also makes it is possible to provide a long oxide superconducting cable conductor having flexibility as well as excellent superconductivity. In the present invention, an eddy current or a coupling current transferred between and flowing across the superconducting tapes is suppressed by the second or subsequent layer of tube-shaped superconductive wires which is provided according to one embodiment of the present invention. The present invention provides a practical AC superconducting cable conductor.

Advantageously the superconductor material is a granulated ceramic inserted into a silver tube which is then drawn to about 1 to about 2 mm. A number, depending on the desired capacity of the final cable, of these small drawn tubes are then inserted into a silver tube which is drawn to the desired

size for use. Optionally, such tube may first be cut into sections and then added to the second silver tube before drawing. This thin, silver, flat tape-shaped material is from about 80 to about 60 percent silver and about 20 to about 40 percent ceramic by weight, advantageously, about 65 percent silver and about 35 percent ceramic.

The present invention also relates to a novel process or method which produces polymeric tapes suitable for use in a cryogenically operated superconducting power cable and the tapes so produced. The processing includes biaxially orienting either a polyethylene, polypropylene, or polybutylene film which has a maximum dielectric constant of about 3.0 and embossing said film with a random pattern. The combination of low dielectric constant, biaxially oriented, embossed film yields a polymeric material which overcomes the problems of brittleness, crazing, and excessive shrinkage which renders polymeric materials produced by known processes unusable in cryogenically operated power cable systems. In addition, the embossing of the film permits the relatively free flow of dielectric fluid within the cable.

The polyolefin sheet stock is biaxially oriented before use in the cable of the present invention. This involves stretching the sheet to a draw ratio of between about 5 to 1 and about 10 to 1 in the length direction and also orienting the sheet across their width.

The sheet, and tapes obtained therefrom which results from processing polyolefin stock to appropriate draw ratios has numerous qualities which make it superior for cable manufacture. To reduce the tape's tendency to fibrillate, to split over its entire length along a single tear, further processing is desirable. This processing involves a biaxial orientation in the direction across the sheet. This orients the sheet to a ratio of up to about 50% in the cross-sheet direction, and produces tape which is sufficiently biaxially oriented to satisfactorily limit the tendency to fibrillate.

The polyethylene, polypropylene and polybutylene tapes produced from the processing noted above are embossed with a particular pattern under specific conditions to assure proper cable impregnation and heat transfer. The embossing pattern consists of random or irregular channels, primarily directed in the cross machine direction. The tapes are cut from or otherwise obtained from the oriented sheet and may be used as single or multiple layer or laminate tapes.



At the same time the pattern, while it may permit some impregnant flow in both the machine and cross-tape direction, favors cross-tape flow and flow between butt gaps because such flow enhances impregnation from layer to layer and encourages heat transfer by convection. The cable itself is constructed of multiple layers of polyolefin tape, either polyethylene, polybutylene or polypropylene. To facilitate cable bending, different widths of polyolefin tape may be used in the layers. The sizes may progress to larger widths with increased distance from the conductor of the cable.

The polyethylene, polypropylene, or polybutylene film of the present invention has a dielectric constant no greater than about 3.0, with about 2.3 being the preferred maximum. The first processing step consists of biaxial orientation, or drawing, advantageously at a ratio of from about 5:1 to about 6:1 in the machine direction and up to about 2:1 in the cross machine direction. Following orientation, the oriented tape is embossed at a temperature of from about 80°C to about 140°C, which produces on the tape a pattern consisting of irregular or random channels primarily directed in the cross machine direction.

Polymeric tapes which have not undergone the novel processing steps described above have several inherent problems which make them unusable in cryogenically operated superconducting power cable systems. For example, in a liquid nitrogen environment at 77°K, most polymeric tapes become glass hard. This will lead to either tensile failure due to thermal contraction exceeding the inherent elongation or to simple disintegration of the tape. Another problem is crazing in liquid nitrogen. Liquid nitrogen, with a boiling point of 77°K, is known to be a powerful crazing agent for polymers. Crazing usually leads to stress cracking and ultimately fracture of the tape. The biaxial orientation process described above overcomes these problems of brittleness, excessive shrinkage, and crazing.

Many polymers exhibit two distinct modes of yielding. One type of yielding involves an applied shear stress, although the yield phenomenon itself is influenced by the normal stress component acting on the yield plane. The second type of yielding involves yielding under the influence of the largest principal stress. This type of yielding is frequently referred to as crazing, or normal stress yielding. Crazing can be induced by stress or by combined stress and solvent action. It shows generally similar features in all polymers in which it has been observed. Crazing appears to the eye to be a fine, microscopic network of cracks almost always advancing in a direction at right angles to the maximum principal stress. Crazing generally originates on the surface at points of local stress

concentration. In a static type of test, it appears that for crazing to occur the stress or strain must reach some critical value. However, crazing can occur at relatively low stress levels under long-time loading.

It is known from extensive electron microscopic examination of crazed areas that molecular chain orientation has occurred in the crazed regions and that oriented fibrils extend across the craze surfaces.

To aid in the construction of the cable the otherwise highly transparent polyolefin insulating tape advantageously is produced with coloring added. This technique adds significantly to the ability to make a useable cable, because the operator must properly index each subsequent spiral layer of tape with the immediate previous layer. When taping with the typical extremely clear and transparent polyethylene, polybutylene or polypropylene tape, the operator is unable to distinguish the butt gaps of the immediate previous layer from other butt gaps as far as eight or ten tape layers beneath. The addition of selected color dyes in specific quantities adds enough color to the tape to permit the operator to easily distinguish the edges, the butt gaps, of the immediate previous layer of tape from those of the earlier layers because the darkness of the color increases significantly with each layer. This coloring agent is selected so as to minimize any increase in dissipation factor of the original material.

The width of the tapes may vary, narrow near the conductor and wider at the outside. The direction of lay may also be reversed at a certain radial thickness, a factor which depends on the design of the taping machine.

The dielectric tapes may be wound in overlapping spiral layers so that each butt gap between spirals of the same layer is offset from the butt gap of the layer below. This construction is facilitated by the production of the insulating tape containing color.

Polyolefin tapes such as polyethylene, polybutylene and polypropylene, when highly oriented as required for the present invention, are transparent. This clarity becomes a disadvantage when the butt gaps of many layers show through to the surface of, the cable very clearly. The operator then has difficulty distinguishing the butt gap of the immediate previous layer, from which each new butt gap

must be offset, from other butt gaps deeper within the cable.

The tape of the present invention therefore has a color component added to it so that the deeper a layer is within the cable, the darker it appears. Organic dyes may be used to produce this color because these organic compounds, unlike inorganic metal salts, have less detrimental effect on the loss tangent and permittivity of the tape.

Since a balance between the needed color and effects on the electrical characteristics must be struck, organic dyes are added in the proportions ranging between 100 to 1000 parts per million.

This results in a reduction in the light transmission of the tape to 10 to 50 percent of the original transmission. When the tape is used on a cable this reduces the visibility to one to four layers, whereas without color, butt gaps as deep as eight to ten layers within the insulation are, still visible.

Orientation is accomplished in the machine direction by stretching or tentering of the sheet to produce a thickness reduction ratio of between 5 to 1 and 10 to 1.

The thickness reduction ratio is in fact a measurement of the linear sheet orientation and is an indication of the changing tensile characteristics of the polymer. The process is advantageously performed at temperatures of between about 80°C and about 140°C.

The sheet is also processed to orient it in the cross-sheet direction to a reduction ratio of up to 50%. This is necessary because without such processing polymers tend to fibrillate, that is, to separate into individual fibers across their width and cause the tape to split lengthwise.

Polyolefin tapes resulting from the processing specified above, however, have a tensile modulus of at least 250,000 psi in the length (machine) direction, and meet all the criteria required for cable manufacture.

The tensile strength attained by the tapes through the processing is not only an indication of the resistance to deterioration, but also a necessity for the use on cable taping machines. Tapes processed as described above can therefore be used on conventional cable making machines with

tensions great enough to construct a satisfactory tightly wound cable.

Before final construction into a cable, the polyolefin tape is embossed to furnish spacing between the tape layers which will facilitate relatively free flow of impregnants within the cable to enhance heat transfer.

These goals are accomplished by a specific embossing technique. The tape is embossed advantageously by rollers. A typical pattern of embossing is shown in FIG. 4 which is a top view of a small section of tape 60 with valleys 61 in the pattern shown as dark lines.

The embossing pattern is characterized as irregular and preferentially permitting cross-tape flow of impregnant as opposed to flow along the length of the tape. The pattern of irregular valleys running essentially across the tape width as seen in FIG. 4 meets these criteria and, unlike a pattern of regular grooves or channels, it can not interlock adjacent tape layers. Non-uniform and irregular patterns therefore assure that the various tape layers can move small distances relative to each other and yield the degree of flexibility required to manufacture and install the cable.

The cross-flow favoring pattern provides heat transfer and impregnation capabilities for the cable. Although it is well understood that polymers are not permeable, the mechanism available for impregnation and heat transfer in the present cable does not depend upon the permeability of the material itself.

The embossed pattern is such that it can increase the effective tape thickness, that is, the peak to peak thickness may be twice the distance of the original tape thickness. The tape is then compressed during winding. Embossing is accomplished by rollers which cause a depression in one surface of the tape and a protrusion in the other surface. Once wound into a cable, these surface irregularities separate the tape layers; but since the pattern favors across-the-tape flow, impregnants need only flow, at the most, one-half the width of the tape to or from a butt gap where it can then progress to the next space between the tapes. This results in a relatively short path from the outside of the cable to the conductor.

Two typical patterns of embossing are: a coarse pattern with a typical 0.1mm mid-height width of the valleys and a typical 0.2mm spacing between adjacent peaks; and a fine pattern with typical 0.025mm mid-height valley widths and typical 0.05mm spacing between peaks.

The availability of embossing patterns ranging from coarse to fine allows the cable designer to strike a compromise between heat transfer and operating stress. The coarse pattern provides the best heat transfer with some reduction in operating voltage stress compared to the fine pattern and vice versa.

One embodiment of the present invention is a process by which semicrystalline polymers are solvent welded using supercritical carbon dioxide. The carbon dioxide acts as a reversible plasticizing agent and does so without interrupting the polymer's morphology or crystal structure. The inventive process can solvent weld highly oriented LLDPE films into a quasi-isotropic laminated film. The mechanical properties of these films were examined and characterized via tensile tests and tear resistance techniques, and in all cases the laminates showed increased properties in all directions as compared to unoriented LLDPE films. There is a synergistic increase in tear resistance of the laminates as compared to the single oriented films.

The present invention includes a method of fabricating quasi-isotropic laminated films from polymer films which allows the laminated film to substantially retain the physical and mechanical properties of the unlaminated film comprising the steps of providing at least two films of a polymer to be laminated; inserting the films into an apparatus adapted to exert force on the films surfaces and to allow contact of the films by a supercritical fluid; bringing the surfaces to be laminated of each of the films into contact; exerting a force on the films thereby urging the film surfaces into contact; contacting the films with a supercritical fluid while the film surfaces are under the exerted force, and allowing the films under the exerted force to remain in the presence of the supercritical fluid for a time and at a temperature sufficient to laminate the surfaces. Advantageously, the polymer is selected from the group consisting of low density and high density polymers. More advantageously, the polymer is selected from the group consisting of poly alkyls having from 2 to 6 carbon atoms. Further, the polymer may be linear or branched. The present invention includes films of the same polymer and films of different polymers. Advantageously, the apparatus used is essentially air tight. Preferably the films of this invention are oriented before being brought into contact. Advantageously the supercritical fluid allows chemical reactions between the polymers of the films. Preferably the

supercritical fluid only permeates the amorphous regions of the polymer and most preferably the supercritical fluid dissolves the amorphous regions of the polymer. The most preferred supercritical fluid is CO<sub>2</sub>. In the method of the present invention the physical and mechanical properties of the resulting laminated film may exceed the physical and mechanical properties of the non-laminated polymer films. The most preferred polymer used in the present invention is a low density polyethylene.

The present invention includes the method of fabricating quasi-isotropic laminated films from polymer films which allows the laminated film to substantially retain the physical and mechanical properties of the unlaminated film comprising the steps of providing at least two films of a polymer to be laminated; providing an enclosed means adapted to exert a force on a film's surface; inserting the films into the enclosed means; bringing the surfaces to be laminated of each of the films into contact; exerting a force on the films thereby urging the film surfaces into contact; contacting the films with a supercritical fluid while the film surfaces are under the exerted force, and allowing the films under the exerted force to remain in the presence of the supercritical fluid for a time and at a temperature sufficient to laminate the surfaces.

This invention further includes laminated films produced by the above methods. Advantageously the laminated films produced by the present method have from 2 to 16, preferably from 2 to 8, layers of polymer film.

In the present invention the laminated films were processed in a high pressure apparatus, shown on Figure 5, specifically designed to allow the application of force to the samples while in the presence of SC CO<sub>2</sub> under controlled temperature. The apparatus was machined from 316 stainless steel and mounted in a PHI hydraulic press. Coleman grade CO<sub>2</sub> was supplied via an inlet port on the apparatus by a Hydro-Pac, Inc. high pressure carbon dioxide pump and filtered through activated carbon and a drying agent. The CO<sub>2</sub> pressure was controlled via a Tescom ER3000 electronic pressure regulator with a computer interface. The ER3000 allows for exact control of CO<sub>2</sub> pressure as well as rate of pressurization or depressurization. Thermocouples penetrate the body of the apparatus and are connected to an Omega PID temperature controller. Unless otherwise specified, all laminated films were processed with an initial normal force of 20,000 lbs (~ 1600psi) and a CO<sub>2</sub> pressure of 1500 psi. The temperature was ramped from 23°C to 95°C over a period of 1h, then

cooled to 23°C overnight while depressurizing at a very slow rate. Eight (8)-ply quasi-isotropic laminated films were welded in a (0,45,90,-45)<sub>2S</sub> lay-up sequence. This configuration produces a symmetric quasi-isotropic laminated film.

LLDPE (30% crystalline by Differential Scanning Calorimetry, DSC) was obtained in the form of a 76 µm thick film. These are metallocene films with an  $M_w$  of 118,400 and a Polydispersity Index (PDI) of 2.79. The film originally has a minimal Hermans orientation function value in the machine direction of  $4.28 \times 10^{-5}$  as based on measured birefringence and a maximum theoretical birefringence of 0.06 for LLDPE. The as received film was oriented further by subsequent drawing at either 127 mm/min or 380 mm/min to a draw of either two or five respectively. The Hermans orientation function value after drawing was determined both via birefringence and wide angle X-ray scattering (WAXS).

Adhesion measurements were made using a 90° Peel Test geometry on an Instron model 1123 with a 100N load cell. Test specimens were 2.54 cm wide and the test rate was 50 mm/min. The tear resistance of the laminated films was evaluated using a single specimen  $J_{IC}$ . The  $J$  values were calculated as follows:

$$J = -\frac{1}{B} \left( \frac{dU}{da} \right)_{\delta} \quad (1)$$

where  $B$  is the thickness of the film,  $a$  is the crack length and  $U$  is the strain energy. The strain energy for the system was calculated from the load vs. displacement curve.  $J_{IC}$  is then defined as the critical energy at which crack propagation first occurs, this value is determined by extrapolation of the linear portion of the  $J$  vs. crack length curve to zero crack length.

The single specimen  $J_{IC}$  is a desirable test because of the limited number of samples available for testing. The applicability of the single specimen  $J_{IC}$  to these thin polymer films is investigated by comparing results of single plies obtained using the Method of Essential Work, Mai, Y.W.; Cotterell, B.; Horlyck, R.; Vigna, G. Polym Eng Sci 1987, 27, 804-809 and Mai, Y.W.; Powell, P.J Polym Sci Part B 1991, 29, 785-793. The method of essential work is calculated as follows

$$w_f = w_e l + \beta w_p l^2 \quad (2)$$

where  $\beta$  is a shape factor of the outer plastic zone which depends on the specimen geometry,  $l$  is ligament length,  $w_p$  is the energy for plastic deformation and  $w_e$  is the energy for elastic deformation. Therefore, from a plot of specific total fracture work vs. ligament length for several specimens one can determine  $w_e$ , a material constant. Although the Method of Essential Work has a more sound theoretical footing for these types of films, the drawback is the need to prepare up to ten identical specimens with varying ligament lengths.

Tear properties were tested in a center notch Mode I geometry with an Instron model 4411 with either a 100N or 5kN load cell at a rate of 2 mm/min. Puncture behavior was measured on an Instron Dynatup Impact test machine fitted with a 6.3 mm tup. The impact zone for the puncture tests was a 3.8 mm diameter circular region. Crystallinity was determined via DSC using 5mg samples at a heating rate of 10°C/min. Birefringence measurements were made on an Olympus polarizing microscope equipped with a 1-20 $\lambda$  Berek compensator. The retardation was measured by using the U-CTB Berek compensator. Wide angle X-ray scattering (WAXS) was measured on a GADDS instrument. Hermans Orientation Function Values were calculated for the birefringence data as follows:

$$f = \frac{\Delta n}{\Delta n_o} \quad (3)$$

where  $\Delta n$  is the measured birefringence and  $\Delta n_o$  is the theoretical maximum birefringence for the material. The Hermans Orientation function for the WAXS was calculated by:

$$f = \frac{3 \langle \cos^2 \phi \rangle - 1}{2} \quad (4)$$

where  $\langle \cos^2 \phi \rangle$  is the average angle that the chains make with the director, which is the average direction of orientation of the chains. The Hermans Orientation Function has values from  $-1/2$  to 1, 1 being perfectly oriented, 0 being without orientation, and  $-1/2$  being orientation perpendicular to the director.

Various aspects of the SC CO<sub>2</sub> welding technique were investigated including the effect of SC CO<sub>2</sub> on morphology and crystal structure. The effects of temperature and presence of SC CO<sub>2</sub> are related to strength of adhesion. The mechanical properties of some quasi-isotropic laminates are also discussed in some detail.



In order to identify appropriate solvent welding conditions, preliminary studies were conducted to characterize the effect of SC CO<sub>2</sub> immersion time on film morphology. Highly oriented single films (DR2 or DR5), were placed in SC CO<sub>2</sub> at elevated temperatures for 1.5h and the Hermans orientation measured via birefringence and WAXS before and after (Table 1). As evidenced by the data in Table 1 there was essentially no difference in the molecular orientation before and after treatment with SC CO<sub>2</sub> at 95°C.

SC CO<sub>2</sub> has been reported to induce annealing of crystallites in some semi-crystalline polymers such as PET, therefore it was necessary to evaluate any effect of SC CO<sub>2</sub> on the crystal structure of the LLDPE. In order to quantify any effects on the crystal structure of LLDPE a series of DSC experiments were conducted as shown in Figure 6. Table 2 gives the percent crystallinity for each experiment as well as the melting temperature.

As illustrated by Table 2 there was no effect on either the percent crystallinity or the melt temperature in SC CO<sub>2</sub> at 95°C for 1.5h. However some annealing effects do occur at extremely long exposure times. The dual melting peak in the as received LLDPE has been attributed to segregation of chains which do not have truly random distributions of chain branches either intra- or inter- molecularly. This minor peak disappears after drawing, evidence of the destruction and reformation of crystallites during the drawing process. This minor peak is seen to reappear when the drawn films are melted and reanalyzed.

The melting temperature of LLDPE is 118°C by DSC. When films are processed as described above it is apparent that no adhesion is measurable between films at temperatures below 85°C in either normal melt pressing conditions, or in the presence of SC CO<sub>2</sub>. However as the temperature is increased above 85°C the adhesive strength increases between the films. The increase in adhesion with temperature is considerably faster in the presence of SC CO<sub>2</sub>, this allows attainment of higher adhesion values at a given temperature. The ability to attain this adhesion at temperatures below the melting temperature allows for the retention of the original morphology and crystal structure after processing.

Wide angle X-ray scattering was performed on both the laminated films as well as the single plies. Some results of the orientation calculations have been mentioned earlier. The d spacings are consistent with the standard orthorhombic unit cell of LLDPE. For the DR2 films only the 110 and the 200 reflections are discernable. The WAXS pattern for the laminated film shows the 8 fold symmetry indicative of its quasi-isotropic nature (Figure 7). The contribution from each individual oriented film was apparent which is further evidence of the retention of morphology in this process.

Results of tensile tests on the laminated films were compared to the oriented individual plies with their orientation perpendicular and parallel to the load direction (Figures 8(a), 8(b)). The laminated films gave similar results for all testing directions, i.e., transversely isotropic. The results of these tests are summarized in Table 3. The initial modulus for the laminated films are only slightly higher than the parallel individual ply, while the strain to failure is significantly higher. The total strain energy density at failure is also significantly higher, being 56% higher than the strain energy density of the parallel film. Data for both the draw ratio 2 and the draw ratio 5 films are presented in Figures 8a and 8b. The draw ratio 5 films show a significant increase in modulus over the draw ratio 2, as is expected, while the strain energy density to failure is decreased, due to a significantly decreased strain to failure. In all cases failure occurred without delamination of the laminated films.

The multi-specimen Method of Essential Work is a solid theoretical basis for the calculation of tear resistance in polymer films, a single specimen approach is preferred so as to limit sample preparation. Yiu-Wing Mai and Powell, Mai, Y.W.; Cotterell, B.; Horlyck, R.; Vigna, G. Polym Eng Sci 1987, 27, 804-809 and Mai, Y.W.; Powell, P. J Polym Sci Part B 1991, 29, 785-793, and others have conducted studies directed toward comparing the results of the Method of Essential Work to a single specimen  $J_{IC}$  and have attained good agreement. The Method of Essential Work and the single specimen  $J_{IC}$  were studied as they pertain to highly oriented LLDPE films in order to assess the practicality of using the single specimen  $J_{IC}$  to characterize quasi-isotropic laminated films. The LLDPE single films were tested in a center notch mode I geometry. Three specimen types were tested, the unoriented film, and the highly oriented single ply with orientation perpendicular and parallel to the load direction. These tests were all conducted on films with draw ratio 2. The results of these tests are listed in Table 4. It is apparent that orientation in polymer films has a profound effect on tear resistance. The films with orientation parallel to the load direction (crack growth perpendicular to orientation), have quite high tear resistance. However for the films with orientation

transverse to the load (crack growth parallel to orientation), there is almost no resistance to crack growth. It is apparent from these studies that in order to resist tear in these oriented films a composite of these two geometries must be created, so as to improve the properties of the films overall.

The data herein suggests a good agreement between the single specimen  $J_{IC}$  and Method of Essential Work for the single plys, therefore a  $J_{IC}$  analysis is appropriate for the 8 ply laminated films.

**Table 1.** Degree of orientation for the as received film, drawn film (DR2), and for the drawn film after exposure to Supercritical  $CO_2$

| Temperature                            | Birefringence         | $f^*$<br>Birefringence | $f^*$<br>WAXS |
|--|-----------------------|------------------------|---------------|
| As received                            | $2.57 \times 10^{-6}$ | -0                     | -0            |
| As drawn DR2                           | 0.029                 | 0.48                   | 0.32          |
| DR2 after 95°C<br>(1.5h in SC $CO_2$ ) | 0.030                 | 0.50                   |               |

\* Hermans Orientation Function Value

**Table 2.** Percent crystallinity and melting temperature for the as received films,  
Drawn films (DR2) and drawn films exposed to Supercritical CO<sub>2</sub>.

| Sample                             | Tm     | Percent Crystallinity |
|------------------------------------|--------|-----------------------|
| As received                        | 119.75 | 29.5                  |
| As drawn DR2                       | 117.23 | 38.4                  |
| DR2 1.5h @ 95°C in CO <sub>2</sub> | 117.22 | 38.4                  |
| DR2 19h @ 75°C in CO <sub>2</sub>  | 117.05 | 37.1                  |

**Table 3.** Mechanical data from tensile tests on the single plys and the laminated films.

| <i>Sample</i>                        | <i>Modulus<br/>(MPa)</i> | <i>Strain to Failure<br/>(mm/mm)</i> | <i>Stress at<br/>Failure (Mpa)</i> | <i>Strain Energy<br/>Density (kJ/m<sup>3</sup>)</i> |
|--------------------------------------|--------------------------|--------------------------------------|------------------------------------|---|
| <i>DR2 transverse<br/>Single Ply</i> | 42                       | --                                   | --                                 | --  |
| <i>DR2 Parallel<br/>Single Ply</i>   | 52                       | 3.2                                  | 48.6                               | 102.3   |
| <i>DR2 Laminated<br/>Film</i>        | 57                       | 6.9                                  | 33.2                               | 159.1   |
| <i>DR5 Parallel<br/>Single Ply</i>   | 230                      | 1.0                                  | 157                                | 61.9  |
| <i>DR5 Laminated<br/>Film</i>        | 152                      | 1.5                                  | 77                                 | 66.1  |

**Table 4.** Comparison of the Method of Essential Work to the Single Specimen  $J_{1C}$  for the single plys (transverse and parallel) and the as received film.

| Specimen    | $f^*$ | $J_{1C}$ (kJ/m <sup>2</sup> ) | $W_e$ kJ/m <sup>3</sup> ) |
|-------------|-------|-------------------------------|---------------------------|
| Transverse  | 0.5   | 8.9                           | 0.5                       |
| As received | -0    | 40.3                          | 47.97                     |
| Parallel    | 0.5   | 205.7                         | 195.83                    |

\* Hermans Orientation Function Value

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

What is claimed is:

1. A cable employing an oxide superconductor, comprising:

a flexible core member;

a plurality of tape-shaped oxide superconducting wires being laid on said core member with tension of not more than 2 kgf/mm<sup>2</sup> wherein each tape-shaped superconducting wire consisting essentially of an oxide superconductor and a stabilizing metal covering the same,

said plurality of tape-shaped superconducting wires forming a plurality of layers each being formed by laying a plurality of said tape-shaped superconducting wires in a side-by-side manner,

said plurality of layers being successively stacked on said core member without an insulating layer between the plurality of layers and the core member,

said core member providing said superconducting cable with flexibility,

said superconducting cable capable of maintaining a superconducting state at the temperature of liquid nitrogen,

said wires having substantially homogeneous superconducting phases along the longitudinal direction of said wire,

the c-axes of said superconducting phases being oriented substantially in parallel with the direction of thickness of said wire,

said superconducting wires being formed by grains aligned in parallel extending along the longitudinal direction of said wire,

said grains being stacked along the direction of thickness of said wire.

2. The superconducting cable of claim 1 having flexibility such that the superconductivity of said cable does not substantially deteriorate upon bending up to about 50 times the diameter of the cable.

3. The superconducting cable of claim 1, wherein said core member is selected from the group consisting essentially of metals, plastics, reinforced plastics, polymers, and composites.
4. The superconducting cable of claim 1, wherein said core member is a pipe having a surface selected from a spiral groove surface, a web shaped surface, a braid surface, and a mat shaped surface on its exterior which forms a surface for the tape-shaped superconducting wires.
5. The superconducting cable of claim 1, wherein an insulating layer is not present between the plurality of layers.
6. The superconducting cable of claim 5, wherein after the first layer of tape-shaped wires are laid on said core member the subsequent tape-shaped plurality of layers are laid on the surfaces formed by the immediately prior layer of tape-shaped wires.
7. The superconducting cable of claim 1, wherein said wires are twisted within said tape-shaped stabilizing metal covering.
8. The superconducting cable of claim 1, wherein said tape-shaped wires are laid at a lay angle of up to about 90 degrees.
9. The superconducting cable of claim 8, wherein said tape-shaped wires are laid at a lay angle of from about 10 to about 60 degrees.
10. The superconducting cable of claim 9, wherein said tape-shaped wires are laid at a lay angle of from about 20 to about 40 degrees.
11. The superconducting cable of claim 1, further including at least two distinct groups of tape-shaped wire layers.
12. The superconducting cable of claim 11, wherein the lay angle of each successive layer of tape-shaped wires alternate in lay direction or pitch.



13. The superconducting cable of claim 12, wherein each said successive layer consists of at least two tape-shaped wires for a construction of four or more even layers.
14. The superconducting cable of claim 11, wherein a layer of dielectric material separates each of the at least two distinct groups of tape-shaped wire layers.
15. The superconducting cable of claim 11, wherein a layer of dielectric material separates the core member from the layer of tape-shaped wires closest thereto.
16. The superconducting cable of claim 14, wherein the dielectric material is selected from the group consisting of polypropylene, polyethylene and polybutylene.
17. The superconducting cable of claim 11, wherein the at least two distinct groups of tape-shaped wire layers carries approximately equal amounts of the current flowing through the cable.
18. The superconducting cable of claim 11, wherein the first of the two distinct groups of tape-shaped wire layers carries greater than 50 percent of the current flowing through the cable.
19. The superconducting cable of claim 11, wherein the second of the two distinct groups of tape-shaped wire layers carries greater than 50 percent of the current flowing through the cable.
20. The superconducting cable of claim 17, wherein the group of tape-shaped wire layers furthest from the core member provides shielding of the current flowing through the other layers and reduces magnetic fields or eddy currents in the cable.
21. The superconducting cable of claim 1, wherein the stabilizing metal is selected from the group consisting of silver, silver alloys, nickel and nickel alloys.
22. The superconducting cable of claim 1, wherein each of said plurality of layers contains at least 2 tape-shaped wires per layer.

23. The superconducting cable of claim 1, wherein each of said plurality of layers contains at least 4 tape-shaped wires per layer.
24. The superconducting cable of claim 23, including an insulating layer between the second and third layer of said plurality of layers.
25. The superconducting cable of claim 23, including an insulating layer between each second and third layer of said plurality of layers.
26. The superconducting cable of claim 14, wherein the dielectric material has a maximum dielectric constant of about 3.0.
27. The superconducting cable of claim 26, wherein the dielectric material has a maximum dielectric constant of about 2.3.
28. The superconducting cable of claim 14, wherein the dielectric material is biaxially oriented at a ratio of from about 5:1 to about 10:1 in the machine direction.
29. The superconducting cable of claim 28, wherein the dielectric material is biaxially oriented at a ratio of from about 5:1 to about 6:1 in the machine direction.
30. The superconducting cable of claim 28, wherein the dielectric material is further biaxially oriented up to about 2:1 in the cross machine direction.
31. The superconducting cable of claim 28, including embossing the biaxially oriented dielectric material so as to form irregular and/or random channels therein.
32. The superconducting cable of claim 31, wherein the dielectric material is embossed with channels having a depth of from about 0.5 to about 2 ml.
33. The superconducting cable of claim 31, wherein the embossing is performed by a roller at a temperature from about 80°C to about 140°C.

34. The superconducting cable of claim 30, wherein the dielectric tape is embossed in a pattern which preferentially permits impregnant flow across the tape width.
35. The superconducting cable of claim 31, wherein the dielectric tape is embossed in a pattern of irregular hills and valleys running across the tape.
36. The superconducting cable of claim 14, wherein the dielectric tape is produced from material which contains organic color dye in a quantity within the range of 100 to 1000 parts per million.
37. The superconducting cable of claim 31, wherein the dielectric tape is embossed in a pattern which increases the effective tape thickness.
38. The superconducting cable of claim 31, wherein the dielectric tape is embossed in a pattern with up to about 0.2mm spacing between the adjacent peaks.
39. The superconducting cable of claim 38, wherein the dielectric tape is embossed in a pattern with up to about 0.05mm spacing between peaks.
40. The superconducting cable of claim 14, wherein the dielectric tape has a tensile modulus of at least 250,000 psi.
41. A method of fabricating quasi-isotropic laminated films from polymer films which allows the laminated film to substantially retain the physical and mechanical properties of the unlaminated film comprising the steps of:
- a. providing at least two films of a polymer to be laminated;
  - b. inserting the films into an apparatus adapted to exert force on the films surfaces and to allow contact of the films by a supercritical fluid;
  - c. bringing the surfaces to be laminated of each of the films into contact;
  - d. exerting a force on the films thereby urging the film surfaces into contact;
  - e. contacting the films with a supercritical fluid while the film surfaces are under the exerted force, and

- f. allowing the films under the exerted force to remain in the presence of the supercritical fluid for a time and at a temperature sufficient to laminate the surfaces.
42. The method of claim 41 wherein the polymer is selected from the group consisting of low density and high density polymers.
43. The method of claim 42 wherein the polymer is selected from the group consisting of poly alkyls having from 2 to 6 carbon atoms.
44. The method of claim 42 wherein the polymer is linear.
45. The method of claim 42 wherein the polymer is branched.
46. The method of claim 41 wherein the films are of the same polymer.
47. The method of claim 41 wherein the films are of different polymers.
48. The method of claim 41 wherein the apparatus is essentially air tight.
49. The method of claim 41 wherein the films are oriented before being brought into contact.
50. The method of claim 41 wherein the supercritical fluid allows chemical reactions between the polymers of the films.
51. The method of claim 50 wherein the supercritical fluid only permeates the amorphous regions of the polymer.
52. The method of claim 51 wherein the supercritical fluid dissolves the amorphous regions of the polymer.
53. The method of claim 51 wherein the supercritical fluid is CO<sub>2</sub>.

54. The method of claim 41 wherein the physical and mechanical properties of the resulting laminated film exceed the physical and mechanical properties of the non-laminated polymer films.

55. The method of claim 43 wherein the polymer is a low density polyethylene.

56. A method of fabricating quasi-isotropic laminated films from polymer films which allows the laminated film to substantially retain the physical and mechanical properties of the unlaminated film comprising the steps of:

- a. providing at least two films of a polymer to be laminated;
- b. providing an enclosed means adapted to exert a force on a film's surface;
- c. inserting the films into the enclosed means;
- d. bringing the surfaces to be laminated of each of the films into contact;
- e. exerting a force on the films thereby urging the film surfaces into contact;
- f. contacting the films with a supercritical fluid while the film surfaces are under the exerted force, and
- g. allowing the films under the exerted force to remain in the presence of the supercritical fluid for a time and at a temperature sufficient to laminate the surfaces.

57. The method of claim 56 wherein the films are of the same polymer.

58. The method of claim 56 wherein the films are of different polymers.

59. The method of claim 56 wherein the films are oriented before being brought into contact.

60. The method of claim 56 wherein the supercritical fluid allows chemical reactions between the polymers of the films.

61. The method of claim 60 wherein the supercritical fluid only permeates the amorphous regions of the polymer.

62. The method of claim 61 wherein the supercritical fluid is CO<sub>2</sub>.
63. The method of claim 56 wherein the physical and mechanical properties of the resulting laminated film exceed the physical and mechanical properties of the non-laminated polymer films.
64. A laminated film produced by the method of claim 41.
65. A laminated film produced by the method of claim 56.
66. A laminated film produced by the method of claim 41 having from 2 to 16 layers of polymer film.
67. A laminated film produced by the method of claim 56 having from 2 to 16 layers of polymer film.

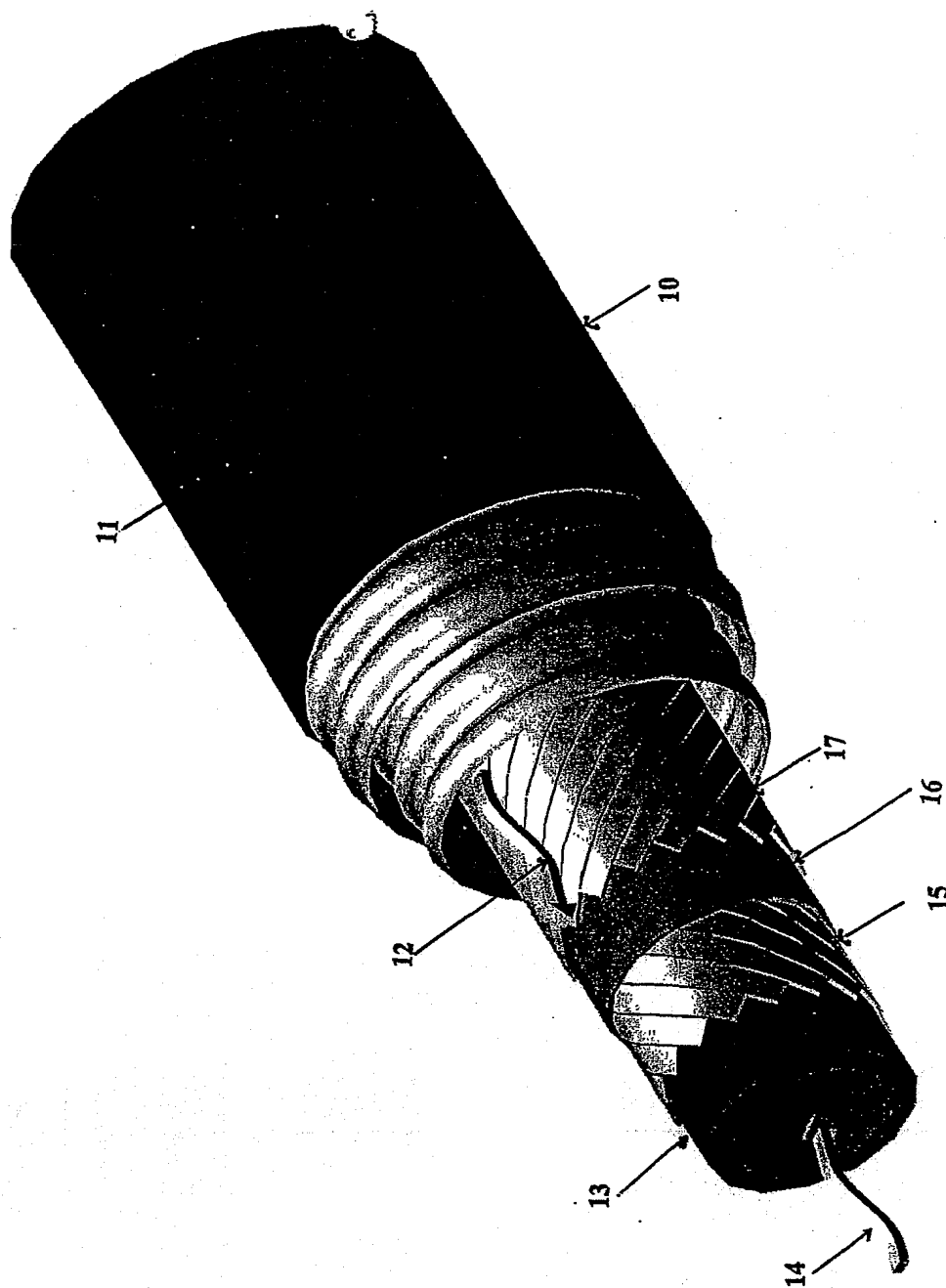


FIGURE 1

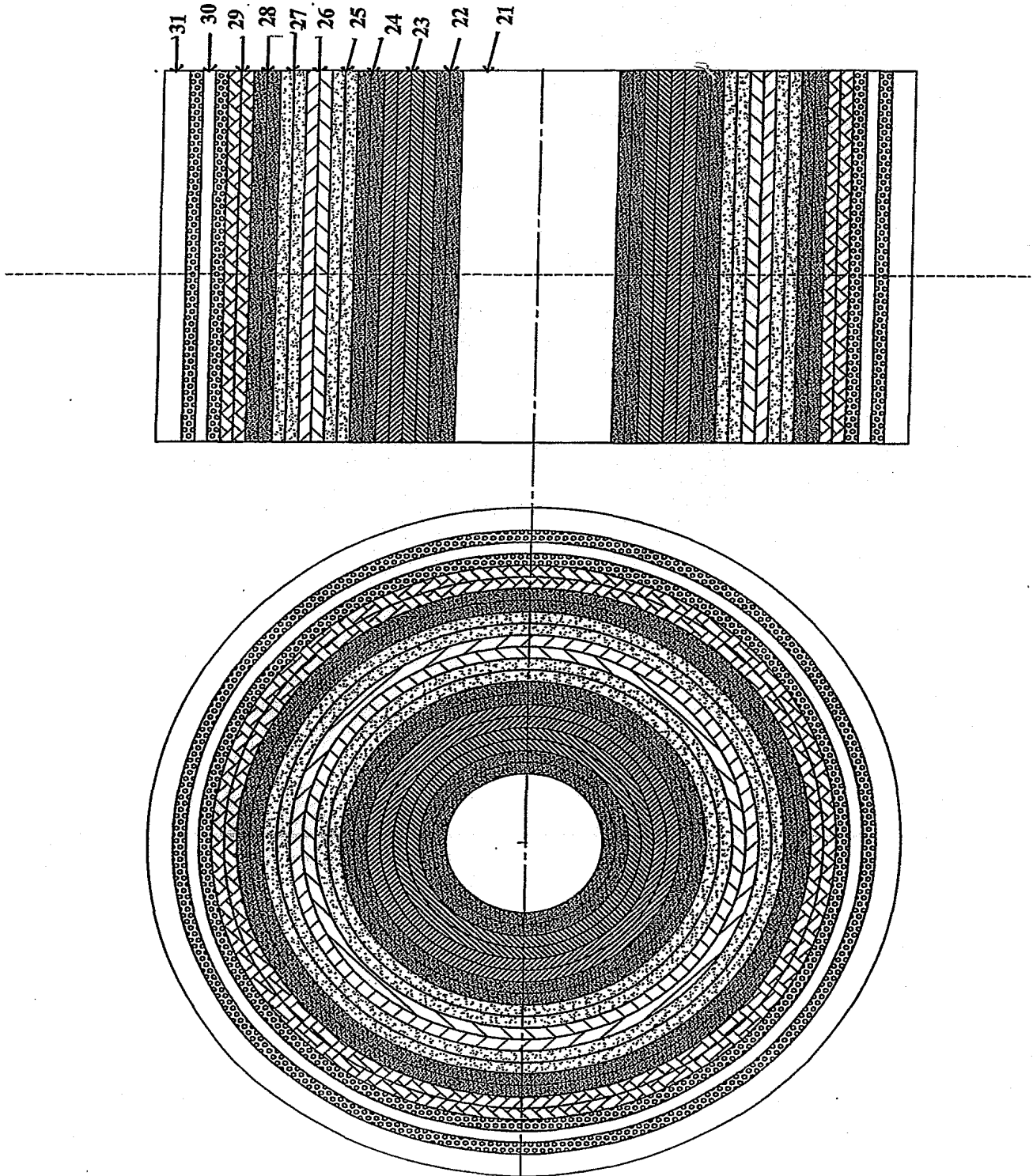


FIGURE 2



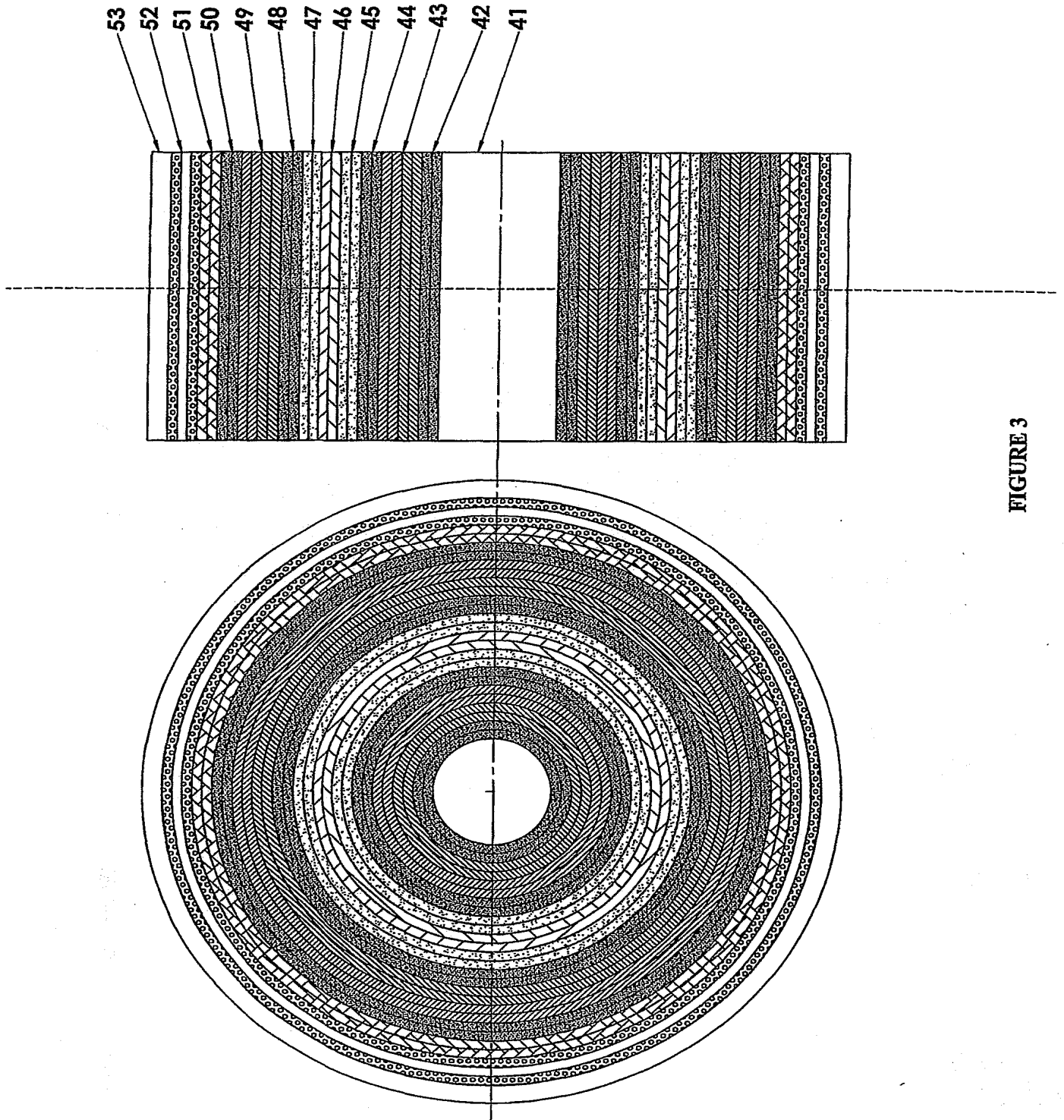


FIGURE 3

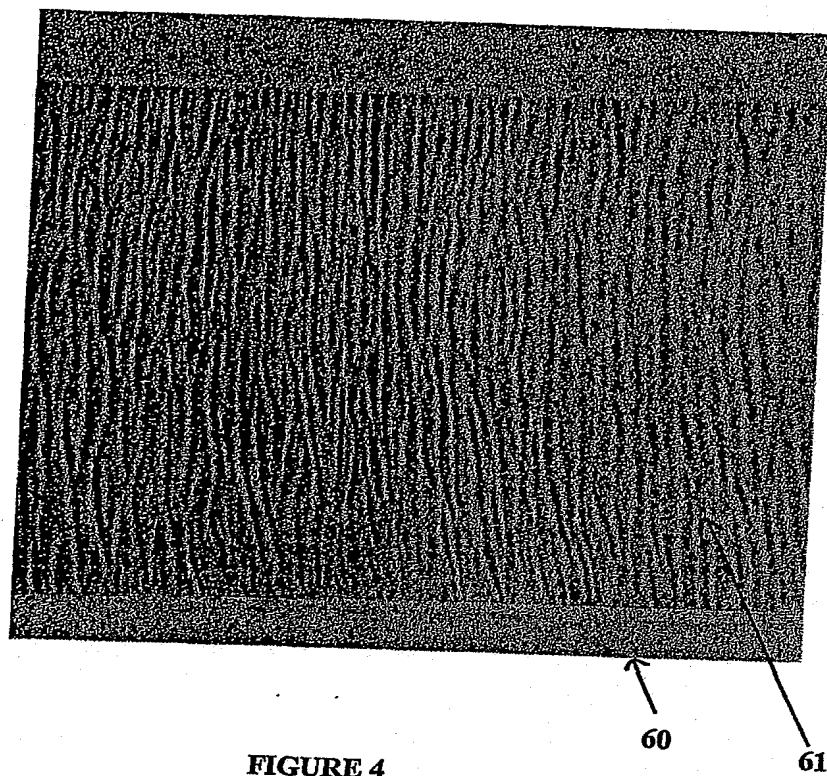


FIGURE 4

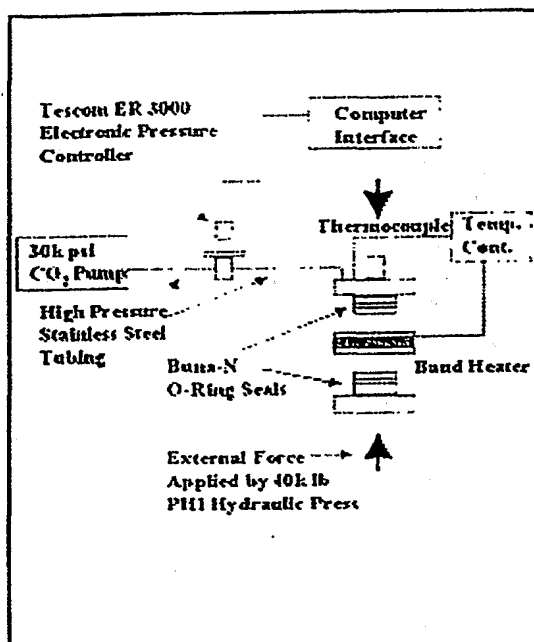
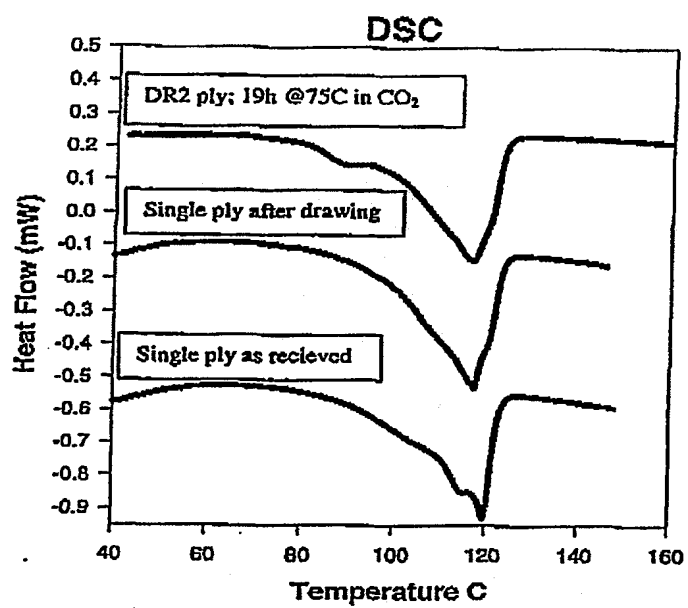
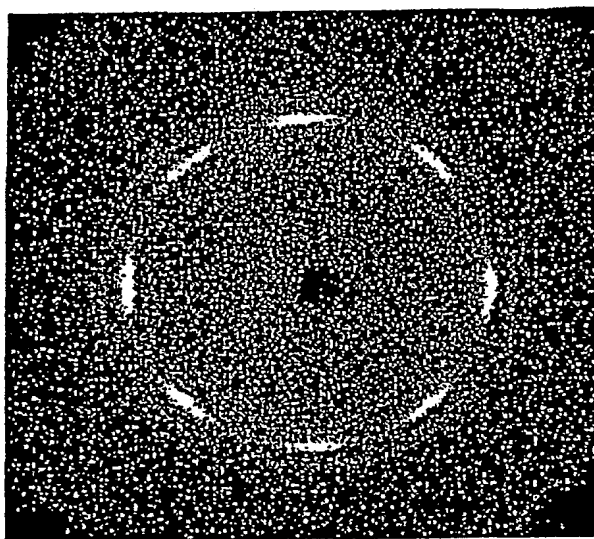


FIGURE 5

**FIGURE 6**



**FIGURE 7**

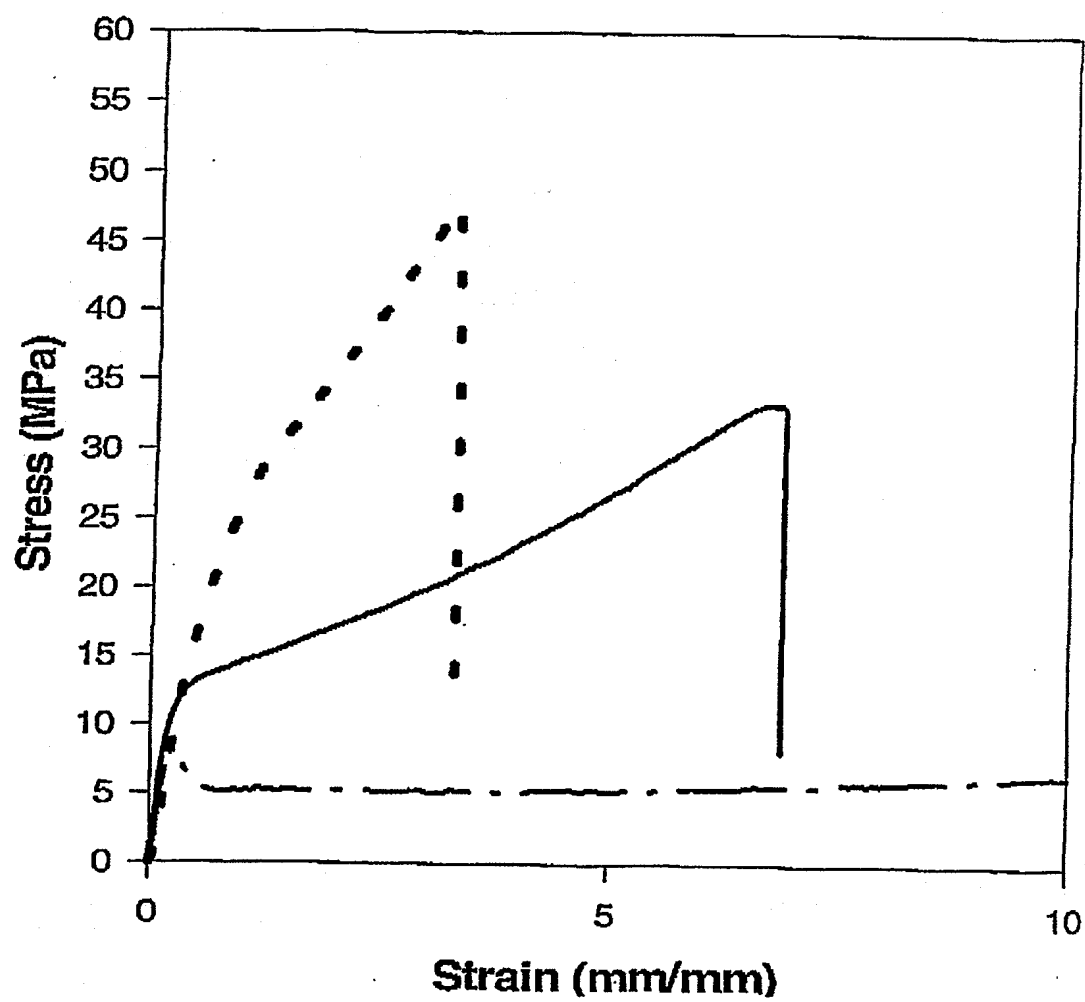


FIGURE 8a

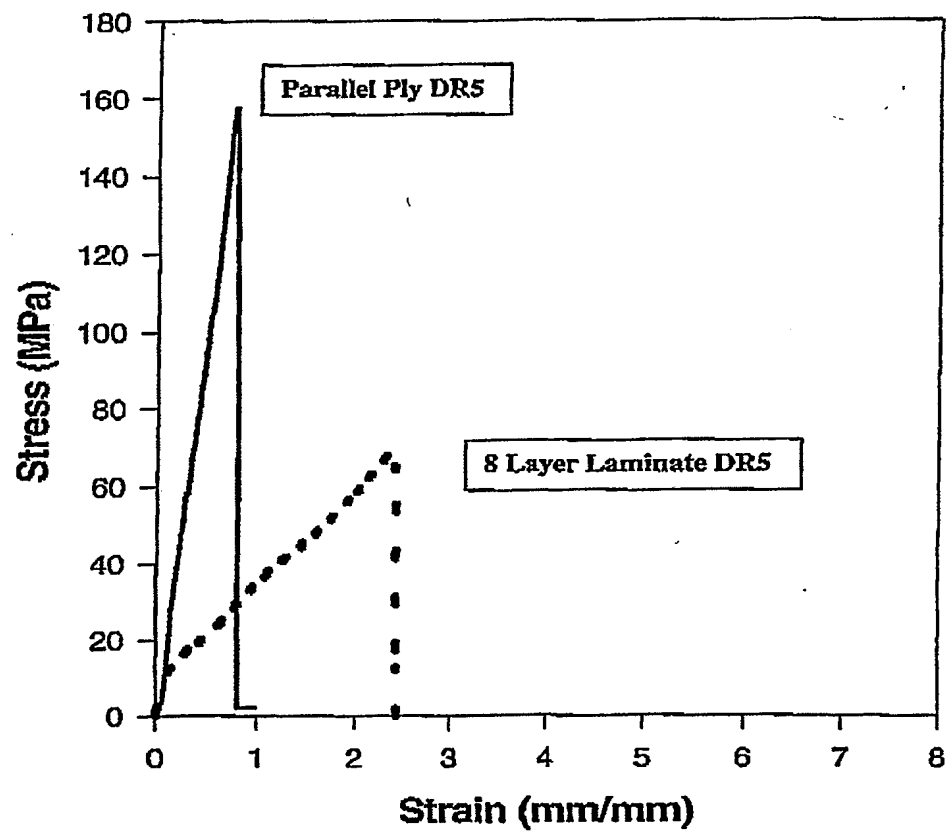


FIGURE 8b

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/28929

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : H01B 12/00

US CL : 174/125.1

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 174/125.1, 505/230, 231, 232, 704

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category *                | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No.   |
|---------------------------|--|---|
| X<br>---<br>Y<br>---<br>A | US 5952614 A (RIES) 14 SEPTEMBER 1999 (14.09.1999), FIG. 4                         | 1, 4-5<br>-----<br>11, 14<br>-----<br>2-3, 6-10, 12-13, 15-67 |
| Y<br>---<br>A             | US 5932523 A (FUJIKAMI et al.) 03 AUGUST 1999 (03.08.1999), FIGS. 3-7              | 11, 14<br>-----<br>1-10, 12-13, 15-67                         |
| A                         | US 3612742 A (SNOWDEN et al.) 12 OCTOBER 1971 (12.10.1971), FIGS. 1-5              | 1-67  |



Further documents are listed in the continuation of Box C.



See patent family annex.

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| "P" document published prior to the international filing date but later than the priority date claimed  |  |

Date of the actual completion of the international search

16 December 2001 (16.12.2001)

Date of mailing of the international search report

03 JAN 2002

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(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
21 March 2002 (21.03.2002)

PCT

(10) International Publication Number  
WO 02/023557 A1

(51) International Patent Classification<sup>7</sup>: H01B 12/00

(21) International Application Number: PCT/US01/28929

(22) International Filing Date:  
14 September 2001 (14.09.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/232,747 15 September 2000 (15.09.2000) US

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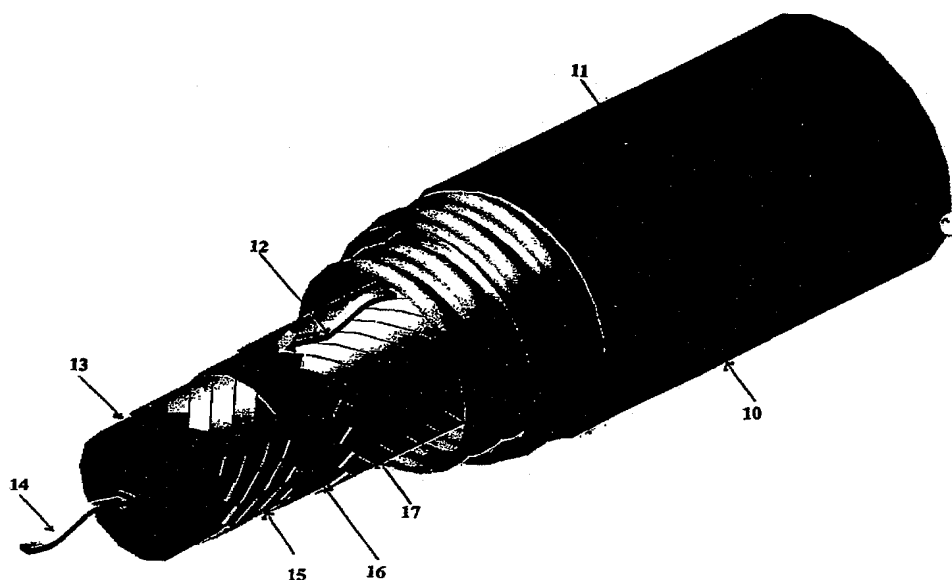
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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European

[Continued on next page]

(54) Title: SUPERCONDUCTING CABLE



(57) Abstract: Tape-shaped superconducting wires (15) include a covering of a stabilizing metal and are wound on a flexible former (13). The superconducting wires are laid on the former (13) at a bending strain of not more than 0.2%. The wires (15) are laid side-by-side to form a first layer. A prescribed number of tape-shaped superconducting wires are laid on top of the first layer side-by-side to form a second layer. The former may be made of a metal, plastic, reinforced plastic, polymer, or a composite and imparts flexibility to the cable.

WO 02/023557 A1



patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(48) Date of publication of this corrected version:

31 July 2003

**Declaration under Rule 4.17:**

— of inventorship (Rule 4.17(iv)) for US only

**Published:**

— with international search report

**(15) Information about Correction:**

see PCT Gazette No. 31/2003 of 31 July 2003, Section II

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

SUPERCONDUCTING CABLE

## BACKGROUND OF THE INVENTION

## FIELD OF THE INVENTION

The present invention relates to a superconducting cable employing a flexible oxide superconductor, and more particularly, it relates to forming a superconducting cable. This invention also relates generally to solvent welding of laminated film and to supercritical solvent welding of oriented films.

## DESCRIPTION OF THE BACKGROUND ART

Superconducting materials are those where the electric resistance approaches zero ( $1\mu\text{v/cm}$ ) below a critical temperature, its value depending on the material. Superconductivity is defined within a critical surface, i.e. a graph or figure with its axes being temperature, electrical current and magnetic field. Thus, for a given working temperature there is a defined curve of critical current which is a function of the magnetic field generated and/or applied to the superconductor.

The best known superconductor materials are NbTi and Nb<sub>3</sub>Sn, however their working temperature is only 4.2K, the boiling temperature of liquid helium. This is the main limitation to large scale application of these superconducting materials. Such superconductors are therefore used almost exclusively for winding of magnets. Manufactured from wires (NbTi and Nb<sub>3</sub>Sn) or tapes (Nb<sub>3</sub>Sn) with high critical current densities ( $3500\text{ A/mm}^2$  5 Tesla for NbTi), such winding of compact magnets provide the production of high fields (up to 18 Tesla) in large volumes.

These superconductor magnets are used for the formation of medical images by nuclear magnetic resonance (MRI) and for materials analysis by the same principle (NMR), the magnets for ore separation and research magnets for high fields, such as those used in large particle accelerators (SSC, HERA, KEK, etc.).

Oxide superconductors of higher critical temperatures were discovered in 1986. These are intermetallic compounds involving metal oxides and rare earths, with perovskite (mica) crystal structure. Their critical temperatures vary from 30K to approaching room temperature and their critical fields are above 60 Tesla. Therefore these materials are considered promising and may replace  $\text{Nb}_3\text{Sn}$  and  $\text{NbTi}$  in the manufacture of magnets and find other applications not feasible with liquid helium, such as transmission of electricity. Such materials have not previously been available as wires, cables, films, tapes or sheets.

An oxide superconductor which enters the superconducting state at the temperature of liquid nitrogen would be advantageous for application in a superconducting cable having a cooling medium of liquid nitrogen. With such an application, it would be possible to simultaneously attain simplification of the thermal protection system and reduction of the cooling cost in relation to a superconducting cable which requires liquid helium.

A superconducting cable must be capable of transmitting high current with low energy loss in a compact conductor. Power transmission is generally made through an alternating current, and a superconductor employed under an alternating current would inevitably be accompanied by energy loss, generically called AC loss. AC losses such as hysteresis loss, coupling loss, or eddy current loss depends on the critical current density of the superconductor, size of filaments, the structure of the conductor, and the like.

Various types of superconducting cables have been experimentally produced using metallic superconductors to study the structures for reducing AC loss, such as a superconductor which comprises a normal conductor and composite multifilamentary superconductors which are spirally wound along the outer periphery of the normal conductor. The conductor is formed by clockwise and counterclockwise wound layers of composite multifilamentary superconductors, which are alternately superimposed with each other. The directions for winding the conductors are varied every layer for reducing magnetic fields generated in the conductors, thereby reducing impedance and increasing current carrying capacity thereof. This conductor has a high-resistance or insulating layer between the layers.

When a cable conductor is formed using an oxide superconductor, the technique employed in a metal superconductor cannot be used. An oxide superconductor, i.e., a ceramic superconductor, is fragile and weak in mechanical strain compared with a metal superconductor. For example, the prior art discloses a technique of spirally winding superconductors around a normal conductor so that the winding pitch is equal to the diameter of each superconductor. However, when a superconducting wire comprising an oxide superconductor covered with a silver sheath is wound at such a short pitch, there is a high probability that the oxide superconductor will be broken, thereby interrupting the current. When an oxide superconducting wire is extremely bent, its critical current may also be greatly reduced.

The cable conductor must be flexible to some extent to facilitate handling. It is also difficult to manufacture a flexible cable conductor from a hard, fragile oxide superconductor.

Polyolefins are the most widely used class of polymers in the world today. They have been made popular by both their useful physical and mechanical properties as well as their inexpensive manufacturability. Because of the inexpensive nature of these polyolefins many attempts have been made to increase the physical and mechanical properties so as to further extend the scope of applications of these polymers. Perhaps the most widely practiced technique for this purpose is orientation. It is well known that upon drawing, the modulus, ultimate strength, tear resistance and puncture resistance are all increased in the draw direction, Ajji, A.; Legros, N.; Dumoulin, M.M. *Advanced Performance Materials* 1998, 5, 117-136. Unfortunately, all of these properties are simultaneously reduced in the transverse direction. Biaxial orientation has led to some degree of success, however the increased material properties are not as significant. It is therefore clear that in order to fully exploit the benefits of orientation, one must find a way to suppress the undesirable decrease in material properties in the transverse direction. One way to accomplish this is to create a quasi-isotropic composite of oriented polyolefins. It would also be beneficial if this could be done without the addition of an adhesive, which itself will serve to change the material properties of the system.

Welding of polymers has received much attention in the polymer community over the last 30 years. The goal of any polymer welding technique is to produce a bond between two polymers (alike or unlike), such that after welding, the weld interface is free of defects and has high structural integrity. Ideally the welded joint will have mechanical and physical properties approaching that of the bulk

polymer. Researchers have developed many methods to weld polymers, all of which have experienced varying degrees of success in practical use.

Perhaps the oldest and most effective procedure for welding polymers involves melt pressing. In this procedure, two polymer substrates are first taken above the melt temperature for semi-crystalline polymers, or above the softening temperature for amorphous polymers. The substrates are then placed in contact with some initial normal force to produce intimate contact and allowed to interdiffuse. In many cases it is possible to produce a welded joint with good mechanical and physical properties. In general, this technique is simple and it is by far the most widely used and effective. Many researchers have extended this simple idea to more elaborate schemes. R. S. Porter and W. T. Mead, Mead, W.T.; Porter, R.S.J. Appl Polym Sci 1978, 22, 3249-3265, have taken this simple concept and created single polymer composites, (composites which are composed of a single type of polymer). By exploiting the difference in melting temperature between High Density Polyethylene (HDPE) fibers (ca. 139°C) and conventional HDPE (ca. 132°C) or Low Density Polyethylene (LDPE) (ca. 110°C), Porter et. al. were able to embed the HDPE fibers into either a HDPE or LDPE matrix, with only minimal relaxation of the fibers. Due to the extremely high degree of orientation in the fibers, they retained a great deal of strength even after relaxation. Similarly, V. Thomas and J. T. Tielking, Thomas, V.; Tielking, J.T.; Wolfenden, A.; Said, M.A. Annu Tech Conf ANTEC Conf Proc 1996, 3, 3234-3238; and Thomas, V.; Said, M.A. Annu Tech Conf ANTEC Conf Proc 1997, 2, 2362-2366, created non-woven fabrics by extruding polymer filaments directly onto a thin polymer film carrier. In both instances the adhesion is due to polymer interdiffusion while in the melt as well as epitaxial transcrystallization. Although this is a very useful and flexible technique, it is always necessary to melt or soften the polymers to the point of flow. Hence, it is normally very difficult to retain any morphology, i.e. crystallinity and orientation, that is in the polymer substrate prior to welding.

Ultrasonic welding is a technique that employs high frequency (10-40 kHz) low amplitude (1-25  $\mu\text{m}$ ) mechanical vibrations to induce cyclical deformation in the polymers. This deformation causes intermolecular friction that converts the mechanical energy to heat. When enough energy has been supplied to overcome the softening temperature, the parts interdiffuse and a weld is achieved, Lin, S.J.; Lin, W.F.; Chang, B.C.; Wu, G.M.; Hung, S.W. Adv Polym Technol 1999, 18, 125-135. Ultrasonic welding is an important process in industry because it is fast and economical. However,

it is best suited to polymers with low softening temperatures and is difficult to adapt to crystalline polymers or polymers with low stiffness. Ultrasonic welding also ultimately relies on thermally induced flow, which means it suffers from most of the drawbacks of conventional melt pressing. Another technique which is widely used for the bonding of polymers is solvent welding. With this technique a solvent or softening agent is applied to the surface of the polymers, and the two surfaces are brought together with an applied force. The adhesion, in this case, is due to diffusion of the solvated/softened material at the interface of the two polymers. C. Y. Yue et. al., Yue, C.Y.; Cherry, B.W. Adhesion (Barking, England) 1986, 147-177, reviewed the structure and strength of solvent welded joints. Yue notes that even after elaborate drying procedures and very long drying times (days to weeks) some solvent always remains in the polymer. This solvent remains in the vicinity of the bond and has a deleterious effect on the strength of the material at that point. Yue found that the bond strength was directly related to the size of this solvent affected region. More recently F. Beaume and N. Brown, Beaume, F.; Brown, N. Journal of Adhesion 1993, 43, 91-100, have studied the solvent welding of polyamide - 11. They too found that the strength of the bond was effected by this solvent affected region, and that since the solvent could never be fully removed, initial material strength could not be attained. In addition to the mechanical effects of this residual solvent, it should also be noted that this technique often employs halogenated solvents, which are highly regulated and must be treated as hazardous waste. This leads to the solvent welded polymers themselves often being treated as hazardous waste due to the residual solvent. Most solvent welding has traditionally been restricted to amorphous polymers, and has found little or no use with crystalline or semi-crystalline polymers.

In recent years, supercritical carbon dioxide (SC CO<sub>2</sub>) has received much attention in the polymer community due to its unique solvent properties. The scope of the field is described in a recent review paper by Andrew I. Cooper, Cooper, A.I. Journal of Materials Chemistry 2000, 10, 207-234. Although supercritical CO<sub>2</sub> is a non-solvent for most polymers, it plasticizes most polymers very efficiently. McCarthy et. al., Kung, E.; Lesser, A.J.; McCarthy, T.J. Macromolecules 1998, 31, 4160-4169, have shown that the increased free volume in the swollen polymers is actually sufficient to allow chemical reactions within the bulk of a polymer. This increase in free volume leads to a decrease in viscosity and hence an increase in chain mobility. Lesser et. al., Hobbs, T.; Lesser, A.J.; J Polym Sci Part B 1999, 37, 1881-1891, have exploited this effect in the drawing of fibers, attaining higher draw ratios than are attainable under ambient conditions. It is important to note that the

carbon dioxide permeates the amorphous regions only, leaving the crystal structure undisturbed, thus allowing semi-crystalline polymers to retain their integrity during and after the process. Because the CO<sub>2</sub> reverts to a gas under ambient conditions, this solvent is easily and completely removed after treatment. This allows SC CO<sub>2</sub> to act as a reversible plasticizing agent.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide a superconducting cable having flexibility and exhibiting excellent superconductivity, particularly high critical current and high critical current density, having an oxide superconductor.

Another object of the present invention is to provide such a superconducting cable which is reduced in AC loss.

According to the present invention a superconducting cable is provided employing an oxide superconductor, which comprises a flexible core member, and a plurality of tape-shaped oxide superconducting wires which are wound on the core member, without an electric insulating layer between the superconducting wires or between the core member and the superconducting wires. In the inventive conductor, each of the oxide superconducting wires consists essentially of an oxide superconductor and a stabilizing metal covering the same. The plurality of tape-shaped superconducting wires laid on the core member form a plurality of layers, each of which is formed by laying a plurality of tape-shaped superconducting wires in a side-by-side manner. The plurality of layers are successively stacked on the core member. This core member provides the inventive superconducting cable with flexibility. The superconducting cable according to the present invention maintains a superconducting state at the temperature of liquid nitrogen.

The conductor according to the present invention further provides an AC conductor which is reduced in AC loss.



The present invention also includes a novel approach to solvent-welding semi-crystalline polymers wherein supercritical carbon dioxide is used as the plasticizing agent. This process is used to fabricate quasi-isotropic laminated films from highly oriented LLDPE film. The interfacial adhesion between individual plies of the laminate is increased over prior art processes without detriment to other physical and mechanical properties of the laminate.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view showing the multilayer structure of the present invention;

FIG. 2 is a sectional side view showing one embodiment of the present invention;

FIG. 3 is a sectional side view showing another embodiment of the present invention;

FIG. 4 is a depiction of the embossing pattern used in the present invention.

FIG. 5 is a schematic drawing of the Supercritical CO<sub>2</sub> processing chamber. The chamber allows for the application of a normal force to the substrate while in the presence of CO<sub>2</sub>.

FIG. 6 is a Differential Scanning Calorimetry (DSC) for the LLDPE films.

FIG. 7 is a Wide Angle X-Ray Scattering (WAXS) of an 8-layer laminated film showing the 8-fold symmetry indicative of the retention of orientation in each ply.

FIG. 8a depicts the results of tensile tests on (————) 8-layer laminated films with a draw ratio of 2 as compared to its single ply constituents tested both with the (— — —) draw direction and in the (— — —) transverse direction.

FIG. 8b depicts the results of tensile tests on (■■■■) 8-layer laminated films with a draw ratio of 5 as compared to its single ply constituents tested in the (■■■■) draw direction.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to a high temperature superconductor cable which may be used in the shielded or unshielded form of construction. There are many applications where both shielded and unshielded cables serve useful purposes.

A modification of this embodiment is to insulate the cable with dielectrics over the high temperature superconductor tapes and then provide another high temperature superconductor layer over the dielectric. The entire cable is then either introduced into a cryostat of the type described above or a cryostat is constructed over the cable. This coaxial construction forces the magnetic field to stay between the inner and the outer layers of high temperature superconductor tapes. There is substantially no magnetic field outside the high temperature superconductor tapes and therefore there is no eddy current in the outer metallic enclosures. With this construction very large amounts of current can be carried depending upon the number of tapes present in the cable. The limitation in this cable design is that the dielectric remains at the cryogenic temperature and a material which can withstand the cryogenic temperature without any physical and mechanical degradation has to be used. The polymeric dielectric material of one embodiment of the present invention has good physical and mechanical properties at liquid nitrogen and lower temperatures. It has high dielectric strength and high breakdown voltage.

Advantageously the cable of the present invention includes the use of a flexible stainless steel corrugated pipe, which is optionally covered with a wire braid or mesh. Preferably, the corrugated pipe is drilled with holes of a size and pattern to allow the liquid nitrogen to flow into the butt gaps of the high temperature superconductor tapes and flood the dielectric material. The high temperature superconductor tapes are laid in a special manner to simulate two layer construction allowing maximum current to flow through the cable.

The dielectric material advantageously consists of semi-conductive tape, aluminized shield tape, and polymeric dielectric tapes. A typical construction of a shielded cable is shown in Fig. 3. An unshielded cable can be constructed by omitting the outer layers of high temperature superconductor tapes. This cable construction is shown in Fig. 2. The present invention includes both shielded and

unshielded high temperature superconductor cable. The design differs from other known cables in the case of an unshielded cable where an extrusion of dielectric material is performed over the thermal insulation cryostat. The prior art does not disclose any method of construction for shielded high temperature superconductor cable.

Referring to Fig. 1, superconductor cable 10 is shown having flexible, evacuated double walled, outer pipe 11, through which liquid nitrogen, 12, flows to a chiller. Ground-potential superconductive shield material 17 encircles dielectric and shield layer 16, which in turn surrounds current carrying superconductive material 15. The flexible, porous-walled inner pipe, 13, is encircled by superconducting material 15 and provides a central, tube-like portion for transport of liquid nitrogen from the chiller. In one embodiment pipe 13 further has a braided surface that contacts superconductive material 15.

Fig. 2 illustrates an embodiment of an unshielded cable wherein former 21 is surrounded by semiconductive bedding tape 22, upon which is laid superconductive tape 23. Another layer of semiconductive bedding tape 24 surround superconductor tape 23. Shielding layer 25 encircles bedding tape 24 and dielectric layer 26 surrounds shielding layer 25. Dielectric layer 26 is encircled by shield layer 27 which in turn is encircled by semiconductive bedding layer 28. Bedding layer 28 is surrounded by binder tape 29, which is encompassed by centering ring 30, in turn surrounded by jacketed cryostat 31.

Referring to Fig. 3, which shows an embodiment of a shielded cable, jacketed cryostat 53 encompasses centering ring 52, which surrounds binder tape 51, which in turn encircles semiconductive tape 50. Tape 50 encircles superconductive tape 49, which surround semiconductive bedding tape 48, which encompass shielding layer 47. Dielectric 46 encircles shield layer 45, which surrounds semiconductive tape 44. Superconductive tape 43 encircles semiconductive bedding tape 42, which surrounds former 41.

The present invention relates to a cable employing an oxide superconductor comprising a flexible core member, a plurality of tape-shaped oxide superconducting wires laid on said core member with tension of not more than about 2 kgf/mm<sup>2</sup> and a bending strain of not more than about 0.2% on the superconductor, wherein each tape-shaped superconducting wire consists essentially of an oxide

superconductor and a stabilizing metal covering the same, said plurality of tape-shaped superconducting wires forming a plurality of layers each being formed by laying said tape-shaped superconducting wires in a side-by-side manner, said plurality of layers being successively stacked on said core member without an insulating layer between the plurality of layers and the core member, said core member providing said superconducting cable with flexibility, said superconducting cable capable of maintaining a superconducting state at the temperature of liquid nitrogen, said wires having substantially homogeneous superconducting phases along the longitudinal direction of said wire, the c-axes of said superconducting phases being oriented substantially in parallel with the direction of thickness of said wire, said superconducting wires being formed by grains aligned in parallel extending along the longitudinal direction of said wire, said grains being stacked along the direction of thickness of said wire.

The superconducting cable advantageously has flexibility such that its superconductivity does not substantially deteriorate upon bending up to about 50 times the diameter of the cable. It is also advantageous that the core member be selected from the group consisting essentially of metals, plastics, reinforced plastics, polymers, and composites. One embodiment of the superconducting cable provides a core member being a pipe having a spiral groove surface, a web shaped surface, a mat shaped surface, or a braid shaped surface on its exterior which forms a surface for the tape-shaped superconducting wires. The inventive superconducting cable does not have any insulating layer between the plurality of layers of the tape-shaped superconducting wires. Advantageously the tape-shaped wires are laid on said core member with the tape-shaped plurality of layers being laid on the surfaces formed by said immediately prior layer of tape-shaped wires. In another embodiment the wires are twisted within said tape-shaped stabilizing metal covering. Advantageously in the superconducting cable said tape-shaped wires are laid at a lay angle of up to about 90 degrees, advantageously from about 10 to about 60 degrees, and preferably from about 20 to about 40 degrees. One embodiment of the present invention includes a superconducting cable having at least two distinct groups of tape-shaped wire layers. Advantageously the lay angle of each successive layer of tape-shaped wires alternate in lay direction or pitch; and each said successive layer consists of at least two tape-shaped wires. Advantageously, a layer of dielectric material separates each of the at least two distinct groups of tape-shaped wire layers. Preferably, a layer of dielectric material separates the core member from the layer of tape-shaped wires closest thereto. Advantageously, the dielectric material is selected from the group consisting of polypropylene, polyethylene, and

polybutylene. In one embodiment of the present invention the at least two distinct groups of tape-shaped wire layers carries approximately equal amounts of the current flowing through the cable. Also advantageous is where the group of tape-shaped wire layers furthest from the core member provides shielding of the current flowing through the other layers and reduces magnetic fields or eddy currents in the cable. Preferably, the stabilizing metal used in the present invention is selected from the group consisting of silver, silver alloys, and nickel and nickel alloys, which may require a buffer layer.

Included in the present invention is an embodiment in which each tape-shaped multifilamentary oxide superconducting wire has such a structure that is a number of filaments consisting essentially of an oxide superconductor contained in a stabilizing material of silver, silver alloys, nickel and nickel alloys. The oxide superconductor may be prepared from an oxide superconductor such as bismuth, strontium, calcium and copper oxide.

Advantageously, each of said plurality of layers contains at least 2 tape-shaped silver contained wires per layer. Preferably, each of said plurality of layers contains at least 4 tape-shaped wires per layer. One embodiment of the present invention includes an insulating layer between the second and third layer of said plurality of layers. Where there are more than 4 layers, advantageously, an insulating layer is present between each second and third layer of said plurality of layers.

In the inventive conductor, the core member, which is generally called a former, is adapted to hold the tape-shaped superconducting wires at a bending strain of the prescribed range. This former has a length which is required for the superconducting cable conductor, and is provided at the center of the superconducting cable conductor. The former is in a substantially cylindrical or spiral shape so that the tape wires are laid thereon, and generally has a substantially constant diameter along its overall length. The former can consist essentially of at least one material selected from the group consisting of metals such as stainless steel, copper, aluminum and the like and plastics, reinforced plastics and ceramics.

According to the present invention, the former is preferably in the form of a tubular member having flexibility. It is also possible to employ a pipe having a spiral groove (hereinafter referred to as a spiral tube) as a former having sufficient strength and flexibility. A bellows tube having a bellows

may also be employed as a former. Further, the former can also be prepared from a spirally wound material such as a spiral steel strip. Each of these shapes is adapted to provide the former with sufficient flexibility. The flexible former provides the inventive conductor with flexibility. The flexible conductor of the present invention can be taken up on a drum.

When practicing the present invention, it is possible to lay or wind several tape-shaped multifilamentary superconducting wires on the former. The tape wires may be laid in two or more layers while directing a surface thereof to the former. Each layer may be formed by an arbitrary number of the tape wires. When several tape wires are laid on the former in parallel with each other so that the surface of the former is filled up with the tape wires, additional tape wires are further wound thereon. When a sufficient number of tape wires are wound on the first layer of the tape wires as a second layer, a third layer of tape wires are then wound thereon. No insulating layer is provided between each adjacent pair of layers.

In the present inventive method, each tape-shaped multifilamentary oxide superconducting wire is laid or wound on a former having a prescribed diameter at a bending strain or a curvature of a prescribed range and a pitch of a prescribed range. A relatively loose bending is applied to the tape wire along its longitudinal direction. The tape wire which is wound on the former is bent at a bending strain of not more than 0.4%, preferably not more than 0.3%. Superconductivity of the tape wire is not substantially reduced upon bending at a bending strain of such a range, as compared with that in a linear state.

The present invention it is preferable to adjust the pitch and the diameter of the former so that the bending strain of the superconductive wire is not more than 0.2%. Each tape-shaped multifilamentary oxide superconducting wire is preferably wound on the former with tension of not more than  $2 \text{ kgf/mm}^{-2}$  in a range of 0.5 to  $2 \text{ kgf/mm}^{-2}$ .

The core member (former) can be formed by either an electric insulating material or an electric conductor. The electric insulating material is preferable in consideration of reduction in AC loss, while a metal which is a conductor is preferable in consideration of strength. A metal pipe having a spiral groove or a metal bellows tube may be used as the core member for providing the conductor with flexibility while maintaining constant strength. A metal core member can also be employed for

safety in the case of an accidental abnormal current. In this case, it is possible to set optimum resistivity of the core member in consideration of AC loss of the conductor and the core member for the abnormal current.

When a metal pipe, which optionally may have a spiral groove, or a metal bellows tube is employed as the core member, the conductor can further comprise a metal tape which is laid or wound on the core member, and dielectric tape which is laid on a the outside surface of the metal tape. The metal tape can form a smooth surface for covering any grooves of the core member so that the superconducting tapes do not buckle. It is possible to cover any grooves while maintaining flexibility of the core member by laying the metal tape.

According to the present invention, it is possible to employ tape-shaped multifilamentary wires each having twisted filaments. The filaments forming a superconducting multifilamentary tape are twisted at a prescribed pitch. Due to such twisting of the filaments, an induction current flowing between a stabilizing metal and the filaments is parted every twisting pitch into small loops, and hence the value of the current is limited. Thus, generation of Joule heat is suppressed in the stabilizing metal and AC loss is reduced as compared with a superconducting wire having untwisted filaments.

The superconducting cable conductor according to the present invention has such flexibility that its superconductivity is substantially not deteriorated also when the same is bent up to 50 times the diameter of the cable. This conductor can be wound on a drum, to be stored and/or transported.

The present invention also makes it is possible to provide a long oxide superconducting cable conductor having flexibility as well as excellent superconductivity. In the present invention, an eddy current or a coupling current transferred between and flowing across the superconducting tapes is suppressed by the second or subsequent layer of tube-shaped superconductive wires which is provided according to one embodiment of the present invention. The present invention provides a practical AC superconducting cable conductor.

Advantageously the superconductor material is a granulated ceramic inserted into a silver tube which is then drawn to about 1 to about 2 mm. A number, depending on the desired capacity of the final cable, of these small drawn tubes are then inserted into a silver tube which is drawn to the desired

size for use. Optionally, such tube may first be cut into sections and then added to the second silver tube before drawing. This thin, silver, flat tape-shaped material is from about 80 to about 60 percent silver and about 20 to about 40 percent ceramic by weight, advantageously, about 65 percent silver and about 35 percent ceramic.

The present invention also relates to a novel process or method which produces polymeric tapes suitable for use in a cryogenically operated superconducting power cable and the tapes so produced. The processing includes biaxially orienting either a polyethylene, polypropylene, or polybutylene film which has a maximum dielectric constant of about 3.0 and embossing said film with a random pattern. The combination of low dielectric constant, biaxially oriented, embossed film yields a polymeric material which overcomes the problems of brittleness, crazing, and excessive shrinkage which renders polymeric materials produced by known processes unusable in cryogenically operated power cable systems. In addition, the embossing of the film permits the relatively free flow of dielectric fluid within the cable.

The polyolefin sheet stock is biaxially oriented before use in the cable of the present invention. This involves stretching the sheet to a draw ratio of between about 5 to 1 and about 10 to 1 in the length direction and also orienting the sheet across their width.

The sheet, and tapes obtained therefrom which results from processing polyolefin stock to appropriate draw ratios has numerous qualities which make it superior for cable manufacture. To reduce the tape's tendency to fibrillate, to split over its entire length along a single tear, further processing is desirable. This processing involves a biaxial orientation in the direction across the sheet. This orients the sheet to a ratio of up to about 50% in the cross-sheet direction, and produces tape which is sufficiently biaxially oriented to satisfactorily limit the tendency to fibrillate.

The polyethylene, polypropylene and polybutylene tapes produced from the processing noted above are embossed with a particular pattern under specific conditions to assure proper cable impregnation and heat transfer. The embossing pattern consists of random or irregular channels, primarily directed in the cross machine direction. The tapes are cut from or otherwise obtained from the oriented sheet and may be used as single or multiple layer or laminate tapes.



At the same time the pattern, while it may permit some impregnant flow in both the machine and cross-tape direction, favors cross-tape flow and flow between butt gaps because such flow enhances impregnation from layer to layer and encourages heat transfer by convection. The cable itself is constructed of multiple layers of polyolefin tape, either polyethylene, polybutylene or polypropylene. To facilitate cable bending, different widths of polyolefin tape may be used in the layers. The sizes may progress to larger widths with increased distance from the conductor of the cable.

The polyethylene, polypropylene, or polybutylene film of the present invention has a dielectric constant no greater than about 3.0, with about 2.3 being the preferred maximum. The first processing step consists of biaxial orientation, or drawing, advantageously at a ratio of from about 5:1 to about 6:1 in the machine direction and up to about 2:1 in the cross machine direction. Following orientation, the oriented tape is embossed at a temperature of from about 80°C to about 140°C, which produces on the tape a pattern consisting of irregular or random channels primarily directed in the cross machine direction.

Polymeric tapes which have not undergone the novel processing steps described above have several inherent problems which make them unusable in cryogenically operated superconducting power cable systems. For example, in a liquid nitrogen environment at 77°K, most polymeric tapes become glass hard. This will lead to either tensile failure due to thermal contraction exceeding the inherent elongation or to simple disintegration of the tape. Another problem is crazing in liquid nitrogen. Liquid nitrogen, with a boiling point of 77°K, is known to be a powerful crazing agent for polymers. Crazing usually leads to stress cracking and ultimately fracture of the tape. The biaxial orientation process described above overcomes these problems of brittleness, excessive shrinkage, and crazing.

Many polymers exhibit two distinct modes of yielding. One type of yielding involves an applied shear stress, although the yield phenomenon itself is influenced by the normal stress component acting on the yield plane. The second type of yielding involves yielding under the influence of the largest principal stress. This type of yielding is frequently referred to as crazing, or normal stress yielding. Crazing can be induced by stress or by combined stress and solvent action. It shows generally similar features in all polymers in which it has been observed. Crazing appears to the eye to be a fine, microscopic network of cracks almost always advancing in a direction at right angles to the maximum principal stress. Crazing generally originates on the surface at points of local stress

concentration. In a static type of test, it appears that for crazing to occur the stress or strain must reach some critical value. However, crazing can occur at relatively low stress levels under long-time loading.

It is known from extensive electron microscopic examination of crazed areas that molecular chain orientation has occurred in the crazed regions and that oriented fibrils extend across the craze surfaces.

To aid in the construction of the cable the otherwise highly transparent polyolefin insulating tape advantageously is produced with coloring added. This technique adds significantly to the ability to make a useable cable, because the operator must properly index each subsequent spiral layer of tape with the immediate previous layer. When taping with the typical extremely clear and transparent polyethylene, polybutylene or polypropylene tape, the operator is unable to distinguish the butt gaps of the immediate previous layer from other butt gaps as far as eight or ten tape layers beneath. The addition of selected color dyes in specific quantities adds enough color to the tape to permit the operator to easily distinguish the edges, the butt gaps, of the immediate previous layer of tape from those of the earlier layers because the darkness of the color increases significantly with each layer. This coloring agent is selected so as to minimize any increase in dissipation factor of the original material.

The width of the tapes may vary; narrow near the conductor and wider at the outside. The direction of lay may also be reversed at a certain radial thickness, a factor which depends on the design of the taping machine.

The dielectric tapes may be wound in overlapping spiral layers so that each butt gap between spirals of the same layer is offset from the butt gap of the layer below. This construction is facilitated by the production of the insulating tape containing color.

Polyolefin tapes such as polyethylene, polybutylene and polypropylene, when highly oriented as required for the present invention, are transparent. This clarity becomes a disadvantage when the butt gaps of many layers show through to the surface of the cable very clearly. The operator then has difficulty distinguishing the butt gap of the immediate previous layer, from which each new butt gap

must be offset, from other butt gaps deeper within the cable.

The tape of the present invention therefore has a color component added to it so that the deeper a layer is within the cable, the darker it appears. Organic dyes may be used to produce this color because these organic compounds, unlike inorganic metal salts, have less detrimental effect on the loss tangent and permittivity of the tape.

Since a balance between the needed color and effects on the electrical characteristics must be struck, organic dyes are added in the proportions ranging between 100 to 1000 parts per million.

This results in a reduction in the light transmission of the tape to 10 to 50 percent of the original transmission. When the tape is used on a cable this reduces the visibility to one to four layers, whereas without color, butt gaps as deep as eight to ten layers within the insulation are, still visible.

Orientation is accomplished in the machine direction by stretching or tentering of the sheet to produce a thickness reduction ratio of between 5 to 1 and 10 to 1.

The thickness reduction ratio is in fact a measurement of the linear sheet orientation and is an indication of the changing tensile characteristics of the polymer. The process is advantageously performed at temperatures of between about 80°C and about 140°C.

The sheet is also processed to orient it in the cross-sheet direction to a reduction ratio of up to 50%. This is necessary because without such processing polymers tend to fibrillate, that is, to separate into individual fibers across their width and cause the tape to split lengthwise.

Polyolefin tapes resulting from the processing specified above, however, have a tensile modulus of at least 250,000 psi in the length (machine) direction, and meet all the criteria required for cable manufacture.

The tensile strength attained by the tapes through the processing is not only an indication of the resistance to deterioration, but also a necessity for the use on cable taping machines. Tapes processed as described above can therefore be used on conventional cable making machines with

tensions great enough to construct a satisfactory tightly wound cable.

Before final construction into a cable, the polyolefin tape is embossed to furnish spacing between the tape layers which will facilitate relatively free flow of impregnants within the cable to enhance heat transfer.

These goals are accomplished by a specific embossing technique. The tape is embossed advantageously by rollers. A typical pattern of embossing is shown in FIG. 4 which is a top view of a small section of tape 60 with valleys 61 in the pattern shown as dark lines.

The embossing pattern is characterized as irregular and preferentially permitting cross-tape flow of impregnant as opposed to flow along the length of the tape. The pattern of irregular valleys running essentially across the tape width as seen in FIG. 4 meets these criteria and, unlike a pattern of regular grooves or channels, it can not interlock adjacent tape layers. Non-uniform and irregular patterns therefore assure that the various tape layers can move small distances relative to each other and yield the degree of flexibility required to manufacture and install the cable.

The cross-flow favoring pattern provides heat transfer and impregnation capabilities for the cable. Although it is well understood that polymers are not permeable, the mechanism available for impregnation and heat transfer in the present cable does not depend upon the permeability of the material itself.

The embossed pattern is such that it can increase the effective tape thickness, that is, the peak to peak thickness may be twice the distance of the original tape thickness. The tape is then compressed during winding. Embossing is accomplished by rollers which cause a depression in one surface of the tape and a protrusion in the other surface. Once wound into a cable, these surface irregularities separate the tape layers; but since the pattern favors across-the-tape flow, impregnants need only flow, at the most, one-half the width of the tape to or from a butt gap where it can then progress to the next space between the tapes. This results in a relatively short path from the outside of the cable to the conductor.

Two typical patterns of embossing are: a coarse pattern with a typical 0.1mm mid-height width of the valleys and a typical 0.2mm spacing between adjacent peaks; and a fine pattern with typical 0.025mm mid-height valley widths and typical 0.05mm spacing between peaks.

The availability of embossing patterns ranging from coarse to fine allows the cable designer to strike a compromise between heat transfer and operating stress. The coarse pattern provides the best heat transfer with some reduction in operating voltage stress compared to the fine pattern and vice versa.

One embodiment of the present invention is a process by which semicrystalline polymers are solvent welded using supercritical carbon dioxide. The carbon dioxide acts as a reversible plasticizing agent and does so without interrupting the polymer's morphology or crystal structure. The inventive process can solvent weld highly oriented LLDPE films into a quasi-isotropic laminated film. The mechanical properties of these films were examined and characterized via tensile tests and tear resistance techniques, and in all cases the laminates showed increased properties in all directions as compared to unoriented LLDPE films. There is a synergistic increase in tear resistance of the laminates as compared to the single oriented films.

The present invention includes a method of fabricating quasi-isotropic laminated films from polymer films which allows the laminated film to substantially retain the physical and mechanical properties of the unlaminated film comprising the steps of providing at least two films of a polymer to be laminated; inserting the films into an apparatus adapted to exert force on the films surfaces and to allow contact of the films by a supercritical fluid; bringing the surfaces to be laminated of each of the films into contact; exerting a force on the films thereby urging the film surfaces into contact; contacting the films with a supercritical fluid while the film surfaces are under the exerted force, and allowing the films under the exerted force to remain in the presence of the supercritical fluid for a time and at a temperature sufficient to laminate the surfaces. Advantageously, the polymer is selected from the group consisting of low density and high density polymers. More advantageously, the polymer is selected from the group consisting of poly alkyls having from 2 to 6 carbon atoms. Further, the polymer may be linear or branched. The present invention includes films of the same polymer and films of different polymers. Advantageously, the apparatus used is essentially air tight. Preferably the films of this invention are oriented before being brought into contact. Advantageously the supercritical fluid allows chemical reactions between the polymers of the films. Preferably the

supercritical fluid only permeates the amorphous regions of the polymer and most preferably the supercritical fluid dissolves the amorphous regions of the polymer. The most preferred supercritical fluid is CO<sub>2</sub>. In the method of the present invention the physical and mechanical properties of the resulting laminated film may exceed the physical and mechanical properties of the non-laminated polymer films. The most preferred polymer used in the present invention is a low density polyethylene.

The present invention includes the method of fabricating quasi-isotropic laminated films from polymer films which allows the laminated film to substantially retain the physical and mechanical properties of the unlaminated film comprising the steps of providing at least two films of a polymer to be laminated; providing an enclosed means adapted to exert a force on a film's surface; inserting the films into the enclosed means; bringing the surfaces to be laminated of each of the films into contact; exerting a force on the films thereby urging the film surfaces into contact; contacting the films with a supercritical fluid while the film surfaces are under the exerted force, and allowing the films under the exerted force to remain in the presence of the supercritical fluid for a time and at a temperature sufficient to laminate the surfaces.

This invention further includes laminated films produced by the above methods. Advantageously the laminated films produced by the present method have from 2 to 16, preferably from 2 to 8, layers of polymer film.

In the present invention the laminated films were processed in a high pressure apparatus, shown on Figure 5, specifically designed to allow the application of force to the samples while in the presence of SC CO<sub>2</sub> under controlled temperature. The apparatus was machined from 316 stainless steel and mounted in a PHI hydraulic press. Coleman grade CO<sub>2</sub> was supplied via an inlet port on the apparatus by a Hydro-Pac, Inc. high pressure carbon dioxide pump and filtered through activated carbon and a drying agent. The CO<sub>2</sub> pressure was controlled via a Tescom ER3000 electronic pressure regulator with a computer interface. The ER3000 allows for exact control of CO<sub>2</sub> pressure as well as rate of pressurization or depressurization. Thermocouples penetrate the body of the apparatus and are connected to an Omega PID temperature controller. Unless otherwise specified, all laminated films were processed with an initial normal force of 20,000 lbs (~ 1600psi) and a CO<sub>2</sub> pressure of 1500 psi. The temperature was ramped from 23°C to 95°C over a period of 1h, then

cooled to 23°C overnight while depressurizing at a very slow rate. Eight (8)-ply quasi-isotropic laminated films were welded in a (0,45,90,-45)<sub>2s</sub> lay-up sequence. This configuration produces a symmetric quasi-isotropic laminated film.

LLDPE (30% crystalline by Differential Scanning Calorimetry, DSC) was obtained in the form of a 76 µm thick film. These are metallocene films with an  $M_w$  of 118,400 and a Polydispersity Index (PDI) of 2.79. The film originally has a minimal Hermans orientation function value in the machine direction of  $4.28 \times 10^{-5}$  as based on measured birefringence and a maximum theoretical birefringence of 0.06 for LLDPE. The as received film was oriented further by subsequent drawing at either 127 mm/min or 380 mm/min to a draw of either two or five respectively. The Hermans orientation function value after drawing was determined both via birefringence and wide angle X-ray scattering (WAXS).

Adhesion measurements were made using a 90° Peel Test geometry on an Instron model 1123 with a 100N load cell. Test specimens were 2.54 cm wide and the test rate was 50 mm/min. The tear resistance of the laminated films was evaluated using a single specimen  $J_{1C}$ . The  $J$  values were calculated as follows:

$$J = -\frac{1}{B} \left( \frac{dU}{da} \right) \delta \quad (1)$$

where  $B$  is the thickness of the film,  $a$  is the crack length and  $U$  is the strain energy. The strain energy for the system was calculated from the load vs. displacement curve.  $J_{1C}$  is then defined as the critical energy at which crack propagation first occurs, this value is determined by extrapolation of the linear portion of the  $J$  vs. crack length curve to zero crack length.

The single specimen  $J_{1C}$  is a desirable test because of the limited number of samples available for testing. The applicability of the single specimen  $J_{1C}$  to these thin polymer films is investigated by comparing results of single plies obtained using the Method of Essential Work, Mai, Y.W.; Cotterell, B.; Horlyck, R.; Vigna, G. Polym Eng Sci 1987, 27, 804-809 and Mai, Y.W.; Powell, P.J Polym Sci Part B 1991, 29, 785-793. The method of essential work is calculated as follows

$$w_f = w_e l + \beta w_p l^2 \quad (2)$$

where  $\beta$  is a shape factor of the outer plastic zone which depends on the specimen geometry,  $l$  is ligament length,  $w_p$  is the energy for plastic deformation and  $w_e$  is the energy for elastic deformation. Therefore, from a plot of specific total fracture work vs. ligament length for several specimens one can determine  $w_e$ , a material constant. Although the Method of Essential Work has a more sound theoretical footing for these types of films, the drawback is the need to prepare up to ten identical specimens with varying ligament lengths.

Tear properties were tested in a center notch Mode I geometry with an Instron model 4411 with either a 100N or 5kN load cell at a rate of 2 mm/min. Puncture behavior was measured on an Instron Dynatup Impact test machine fitted with a 6.3 mm tup. The impact zone for the puncture tests was a 3.8 mm diameter circular region. Crystallinity was determined via DSC using 5mg samples at a heating rate of 10°C/min. Birefringence measurements were made on an Olympus polarizing microscope equipped with a 1-20 $\lambda$  Berek compensator. The retardation was measured by using the U-CTB Berek compensator. Wide angle X-ray scattering (WAXS) was measured on a GADDS instrument. Hermans Orientation Function Values were calculated for the birefringence data as follows:

$$f = \frac{\Delta n}{\Delta n_o} \quad (3)$$

where  $\Delta n$  is the measured birefringence and  $\Delta n_o$  is the theoretical maximum birefringence for the material. The Hermans Orientation function for the WAXS was calculated by:

$$f = \frac{3 \langle \cos^2 \phi \rangle - 1}{2} \quad (4)$$

where  $\langle \cos^2 \phi \rangle$  is the average angle that the chains make with the director, which is the average direction of orientation of the chains. The Hermans Orientation Function has values from  $-1/2$  to 1, 1 being perfectly oriented, 0 being without orientation, and  $-1/2$  being orientation perpendicular to the director.

Various aspects of the SC CO<sub>2</sub> welding technique were investigated including the effect of SC CO<sub>2</sub> on morphology and crystal structure. The effects of temperature and presence of SC CO<sub>2</sub> are related to strength of adhesion. The mechanical properties of some quasi-isotropic laminates are also discussed in some detail.



In order to identify appropriate solvent welding conditions, preliminary studies were conducted to characterize the effect of SC CO<sub>2</sub> immersion time on film morphology. Highly oriented single films (DR2 or DR5), were placed in SC CO<sub>2</sub> at elevated temperatures for 1.5h and the Hermans orientation measured via birefringence and WAXS before and after (Table 1). As evidenced by the data in Table 1 there was essentially no difference in the molecular orientation before and after treatment with SC CO<sub>2</sub> at 95°C.

SC CO<sub>2</sub> has been reported to induce annealing of crystallites in some semi-crystalline polymers such as PET, therefore it was necessary to evaluate any effect of SC CO<sub>2</sub> on the crystal structure of the LLDPE. In order to quantify any effects on the crystal structure of LLDPE a series of DSC experiments were conducted as shown in Figure 6. Table 2 gives the percent crystallinity for each experiment as well as the melting temperature.

As illustrated by Table 2 there was no effect on either the percent crystallinity or the melt temperature in SC CO<sub>2</sub> at 95°C for 1.5h. However some annealing effects do occur at extremely long exposure times. The dual melting peak in the as received LLDPE has been attributed to segregation of chains which do not have truly random distributions of chain branches either intra- or inter- molecularly. This minor peak disappears after drawing, evidence of the destruction and reformation of crystallites during the drawing process. This minor peak is seen to reappear when the drawn films are melted and reanalyzed.

The melting temperature of LLDPE is 118°C by DSC. When films are processed as described above it is apparent that no adhesion is measurable between films at temperatures below 85°C in either normal melt pressing conditions, or in the presence of SC CO<sub>2</sub>. However as the temperature is increased above 85°C the adhesive strength increases between the films. The increase in adhesion with temperature is considerably faster in the presence of SC CO<sub>2</sub>, this allows attainment of higher adhesion values at a given temperature. The ability to attain this adhesion at temperatures below the melting temperature allows for the retention of the original morphology and crystal structure after processing.

Wide angle X-ray scattering was performed on both the laminated films as well as the single plys. Some results of the orientation calculations have been mentioned earlier. The d spacings are consistent with the standard orthorhombic unit cell of LLDPE. For the DR2 films only the 110 and the 200 reflections are discernable. The WAXS pattern for the laminated film shows the 8 fold symmetry indicative of its quasi-isotropic nature (Figure 7). The contribution from each individual oriented film was apparent which is further evidence of the retention of morphology in this process.

Results of tensile tests on the laminated films were compared to the oriented individual plys with their orientation perpendicular and parallel to the load direction (Figures 8(a), 8(b)). The laminated films gave similar results for all testing directions, i.e., transversely isotropic. The results of these tests are summarized in Table 3. The initial modulus for the laminated films are only slightly higher than the parallel individual ply, while the strain to failure is significantly higher. The total strain energy density at failure is also significantly higher, being 56% higher than the strain energy density of the parallel film. Data for both the draw ratio 2 and the draw ratio 5 films are presented in Figures 8a and 8b. The draw ratio 5 films show a significant increase in modulus over the draw ratio 2, as is expected, while the strain energy density to failure is decreased, due to a significantly decreased strain to failure. In all cases failure occurred without delamination of the laminated films.

The multi-specimen Method of Essential Work is a solid theoretical basis for the calculation of tear resistance in polymer films, a single specimen approach is preferred so as to limit sample preparation. Yiu-Wing Mai and Powell, Mai, Y.W.; Cotterell, B.; Horlyck, R.; Vigna, G. Polym Eng Sci 1987, 27, 804-809 and Mai, Y.W.; Powell, P. J Polym Sci Part B 1991, 29, 785-793, and others have conducted studies directed toward comparing the results of the Method of Essential Work to a single specimen  $J_{IC}$  and have attained good agreement. The Method of Essential Work and the single specimen  $J_{IC}$  were studied as they pertain to highly oriented LLDPE films in order to assess the practicality of using the single specimen  $J_{IC}$  to characterize quasi-isotropic laminated films. The LLDPE single films were tested in a center notch mode I geometry. Three specimen types were tested, the unoriented film, and the highly oriented single ply with orientation perpendicular and parallel to the load direction. These tests were all conducted on films with draw ratio 2. The results of these tests are listed in Table 4. It is apparent that orientation in polymer films has a profound effect on tear resistance. The films with orientation parallel to the load direction (crack growth perpendicular to orientation), have quite high tear resistance. However for the films with orientation

transverse to the load (crack growth parallel to orientation), there is almost no resistance to crack growth. It is apparent from these studies that in order to resist tear in these oriented films a composite of these two geometries must be created, so as to improve the properties of the films overall.

The data herein suggests a good agreement between the single specimen  $J_{IC}$  and Method of Essential Work for the single plys, therefore a  $J_{IC}$  analysis is appropriate for the 8 ply laminated films.

**Table 1.** Degree of orientation for the as received film, drawn film (DR2), and for the drawn film after exposure to Supercritical  $CO_2$

| Temperature                            | Birefringence         | $f^*$<br>Birefringence | $f^*$<br>WAXS |
|--|-----------------------|------------------------|---------------|
| As received                            | $2.57 \times 10^{-6}$ | -0                     | -0            |
| As drawn DR2                           | 0.029                 | 0.48                   | 0.32          |
| DR2 after 95°C<br>(1.5h in SC $CO_2$ ) | 0.030                 | 0.50                   |               |

\* Hermans Orientation Function Value

**Table 2.** Percent crystallinity and melting temperature for the as received films,  
Drawn films (DR2) and drawn films exposed to Supercritical CO<sub>2</sub>.

| Sample                             | Tm     | Percent Crystallinity |
|------------------------------------|--------|-----------------------|
| As received                        | 119.75 | 29.5                  |
| As drawn DR2                       | 117.23 | 38.4                  |
| DR2 1.5h @ 95°C in CO <sub>2</sub> | 117.22 | 38.4                  |
| DR2 19h @ 75°C in CO <sub>2</sub>  | 117.05 | 37.1                  |

**Table 3.** Mechanical data from tensile tests on the single plys and the laminated films.

| <i>Sample</i>                        | <i>Modulus<br/>(MPa)</i> | <i>Strain to Failure<br/>(mm/mm)</i> | <i>Stress at<br/>Failure (Mpa)</i> | <i>Strain Energy<br/>Density (kJ/m<sup>3</sup>)</i> |
|--------------------------------------|--------------------------|--------------------------------------|------------------------------------|---|
| <i>DR2 transverse<br/>Single Ply</i> | 42                       | --                                   | --                                 | --  |
| <i>DR2 Parallel<br/>Single Ply</i>   | 52                       | 3.2                                  | 48.6                               | 102.3   |
| <i>DR2 Laminated<br/>Film</i>        | 57                       | 6.9                                  | 33.2                               | 159.1   |
| <i>DR5 Parallel<br/>Single Ply</i>   | 230                      | 1.0                                  | 157                                | 61.9  |
| <i>DR5 Laminated<br/>Film</i>        | 152                      | 1.5                                  | 77                                 | 66.1  |

**Table 4.** Comparison of the Method of Essential Work to the Single Specimen  $J_{1C}$  for the single plys (transverse and parallel) and the as received film.

| Specimen    | $f^*$ | $J_{1C}$ (kJ/m <sup>2</sup> ) | $W_e$ kJ/m <sup>3</sup> |
|-------------|-------|-------------------------------|-------------------------|
| Transverse  | 0.5   | 8.9                           | 0.5                     |
| As received | -0    | 40.3                          | 47.97                   |
| Parallel    | 0.5   | 205.7                         | 195.83                  |

\* Hermans Orientation Function Value

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

What is claimed is:

1. A cable employing an oxide superconductor, comprising:

a flexible core member;

a plurality of tape-shaped oxide superconducting wires being laid on said core member with tension of not more than 2 kgf/mm<sup>2</sup> wherein each tape-shaped superconducting wire consisting essentially of an oxide superconductor and a stabilizing metal covering the same,

said plurality of tape-shaped superconducting wires forming a plurality of layers each being formed by laying a plurality of said tape-shaped superconducting wires in a side-by-side manner,

said plurality of layers being successively stacked on said core member without an insulating layer between the plurality of layers and the core member,

said core member providing said superconducting cable with flexibility,

said superconducting cable capable of maintaining a superconducting state at the temperature of liquid nitrogen,

said wires having substantially homogeneous superconducting phases along the longitudinal direction of said wire,

the c-axes of said superconducting phases being oriented substantially in parallel with the direction of thickness of said wire,

said superconducting wires being formed by grains aligned in parallel extending along the longitudinal direction of said wire,

said grains being stacked along the direction of thickness of said wire.

2. The superconducting cable of claim 1 having flexibility such that the superconductivity of said cable does not substantially deteriorate upon bending up to about 50 times the diameter of the cable.

3. The superconducting cable of claim 1, wherein said core member is selected from the group consisting essentially of metals, plastics, reinforced plastics, polymers, and composites.
4. The superconducting cable of claim 1, wherein said core member is a pipe having a surface selected from a spiral groove surface, a web shaped surface, a braid surface, and a mat shaped surface on its exterior which forms a surface for the tape-shaped superconducting wires.
5. The superconducting cable of claim 1, wherein an insulating layer is not present between the plurality of layers.
6. The superconducting cable of claim 5, wherein after the first layer of tape-shaped wires are laid on said core member the subsequent tape-shaped plurality of layers are laid on the surfaces formed by the immediately prior layer of tape-shaped wires.
7. The superconducting cable of claim 1, wherein said wires are twisted within said tape-shaped stabilizing metal covering.
8. The superconducting cable of claim 1, wherein said tape-shaped wires are laid at a lay angle of up to about 90 degrees.
9. The superconducting cable of claim 8, wherein said tape-shaped wires are laid at a lay angle of from about 10 to about 60 degrees.
10. The superconducting cable of claim 9, wherein said tape-shaped wires are laid at a lay angle of from about 20 to about 40 degrees.
11. The superconducting cable of claim 1, further including at least two distinct groups of tape-shaped wire layers.
12. The superconducting cable of claim 11, wherein the lay angle of each successive layer of tape-shaped wires alternate in lay direction or pitch.



13. The superconducting cable of claim 12, wherein each said successive layer consists of at least two tape-shaped wires for a construction of four or more even layers.
14. The superconducting cable of claim 11, wherein a layer of dielectric material separates each of the at least two distinct groups of tape-shaped wire layers.
15. The superconducting cable of claim 11, wherein a layer of dielectric material separates the core member from the layer of tape-shaped wires closest thereto.
16. The superconducting cable of claim 14, wherein the dielectric material is selected from the group consisting of polypropylene, polyethylene and polybutylene.
17. The superconducting cable of claim 11, wherein the at least two distinct groups of tape-shaped wire layers carries approximately equal amounts of the current flowing through the cable.
18. The superconducting cable of claim 11, wherein the first of the two distinct groups of tape-shaped wire layers carries greater than 50 percent of the current flowing through the cable.
19. The superconducting cable of claim 11, wherein the second of the two distinct groups of tape-shaped wire layers carries greater than 50 percent of the current flowing through the cable.
20. The superconducting cable of claim 17, wherein the group of tape-shaped wire layers furthest from the core member provides shielding of the current flowing through the other layers and reduces magnetic fields or eddy currents in the cable.
21. The superconducting cable of claim 1, wherein the stabilizing metal is selected from the group consisting of silver, silver alloys, nickel and nickel alloys.
22. The superconducting cable of claim 1, wherein each of said plurality of layers contains at least 2 tape-shaped wires per layer.

23. The superconducting cable of claim 1, wherein each of said plurality of layers contains at least 4 tape-shaped wires per layer.
24. The superconducting cable of claim 23, including an insulating layer between the second and third layer of said plurality of layers.
25. The superconducting cable of claim 23, including an insulating layer between each second and third layer of said plurality of layers.
26. The superconducting cable of claim 14, wherein the dielectric material has a maximum dielectric constant of about 3.0.
27. The superconducting cable of claim 26, wherein the dielectric material has a maximum dielectric constant of about 2.3.
28. The superconducting cable of claim 14, wherein the dielectric material is biaxially oriented at a ratio of from about 5:1 to about 10:1 in the machine direction.
29. The superconducting cable of claim 28, wherein the dielectric material is biaxially oriented at a ratio of from about 5:1 to about 6:1 in the machine direction.
30. The superconducting cable of claim 28, wherein the dielectric material is further biaxially oriented up to about 2:1 in the cross machine direction.
31. The superconducting cable of claim 28, including embossing the biaxially oriented dielectric material so as to form irregular and/or random channels therein.
32. The superconducting cable of claim 31, wherein the dielectric material is embossed with channels having a depth of from about 0.5 to about 2 ml.
33. The superconducting cable of claim 31, wherein the embossing is performed by a roller at a temperature from about 80°C to about 140°C.

34. The superconducting cable of claim 30, wherein the dielectric tape is embossed in a pattern which preferentially permits impregnant flow across the tape width.

35. The superconducting cable of claim 31, wherein the dielectric tape is embossed in a pattern of irregular hills and valleys running across the tape.

36. The superconducting cable of claim 14, wherein the dielectric tape is produced from material which contains organic color dye in a quantity within the range of 100 to 1000 parts per million.

37. The superconducting cable of claim 31, wherein the dielectric tape is embossed in a pattern which increases the effective tape thickness.

38. The superconducting cable of claim 31, wherein the dielectric tape is embossed in a pattern with up to about 0.2mm spacing between the adjacent peaks.

39. The superconducting cable of claim 38, wherein the dielectric tape is embossed in a pattern with up to about 0.05mm spacing between peaks.

40. The superconducting cable of claim 14, wherein the dielectric tape has a tensile modulus of at least 250,000 psi.

41. A method of fabricating quasi-isotropic laminated films from polymer films which allows the laminated film to substantially retain the physical and mechanical properties of the unlaminated film comprising the steps of:

- a. providing at least two films of a polymer to be laminated;
- b. inserting the films into an apparatus adapted to exert force on the films surfaces and to allow contact of the films by a supercritical fluid;
- c. bringing the surfaces to be laminated of each of the films into contact;
- d. exerting a force on the films thereby urging the film surfaces into contact;
- e. contacting the films with a supercritical fluid while the film surfaces are under the exerted force, and

- f. allowing the films under the exerted force to remain in the presence of the supercritical fluid for a time and at a temperature sufficient to laminate the surfaces.
42. The method of claim 41 wherein the polymer is selected from the group consisting of low density and high density polymers.
43. The method of claim 42 wherein the polymer is selected from the group consisting of poly alkyls having from 2 to 6 carbon atoms.
44. The method of claim 42 wherein the polymer is linear.
45. The method of claim 42 wherein the polymer is branched.
46. The method of claim 41 wherein the films are of the same polymer.
47. The method of claim 41 wherein the films are of different polymers.
48. The method of claim 41 wherein the apparatus is essentially air tight.
49. The method of claim 41 wherein the films are oriented before being brought into contact.
50. The method of claim 41 wherein the supercritical fluid allows chemical reactions between the polymers of the films.
51. The method of claim 50 wherein the supercritical fluid only permeates the amorphous regions of the polymer.
52. The method of claim 51 wherein the supercritical fluid dissolves the amorphous regions of the polymer.
53. The method of claim 51 wherein the supercritical fluid is CO<sub>2</sub>.

54. The method of claim 41 wherein the physical and mechanical properties of the resulting laminated film exceed the physical and mechanical properties of the non-laminated polymer films.
55. The method of claim 43 wherein the polymer is a low density polyethylene.
56. A method of fabricating quasi-isotropic laminated films from polymer films which allows the laminated film to substantially retain the physical and mechanical properties of the unlaminated film comprising the steps of:
- a. providing at least two films of a polymer to be laminated;
  - b. providing an enclosed means adapted to exert a force on a film's surface;
  - c. inserting the films into the enclosed means;
  - d. bringing the surfaces to be laminated of each of the films into contact;
  - e. exerting a force on the films thereby urging the film surfaces into contact;
  - f. contacting the films with a supercritical fluid while the film surfaces are under the exerted force, and
  - g. allowing the films under the exerted force to remain in the presence of the supercritical fluid for a time and at a temperature sufficient to laminate the surfaces.
57. The method of claim 56 wherein the films are of the same polymer.
58. The method of claim 56 wherein the films are of different polymers.
59. The method of claim 56 wherein the films are oriented before being brought into contact.
60. The method of claim 56 wherein the supercritical fluid allows chemical reactions between the polymers of the films.
61. The method of claim 60 wherein the supercritical fluid only permeates the amorphous regions of the polymer.

62. The method of claim 61 wherein the supercritical fluid is CO<sub>2</sub>.
63. The method of claim 56 wherein the physical and mechanical properties of the resulting laminated film exceed the physical and mechanical properties of the non-laminated polymer films.
64. A laminated film produced by the method of claim 41.
65. A laminated film produced by the method of claim 56.
66. A laminated film produced by the method of claim 41 having from 2 to 16 layers of polymer film.
67. A laminated film produced by the method of claim 56 having from 2 to 16 layers of polymer film.

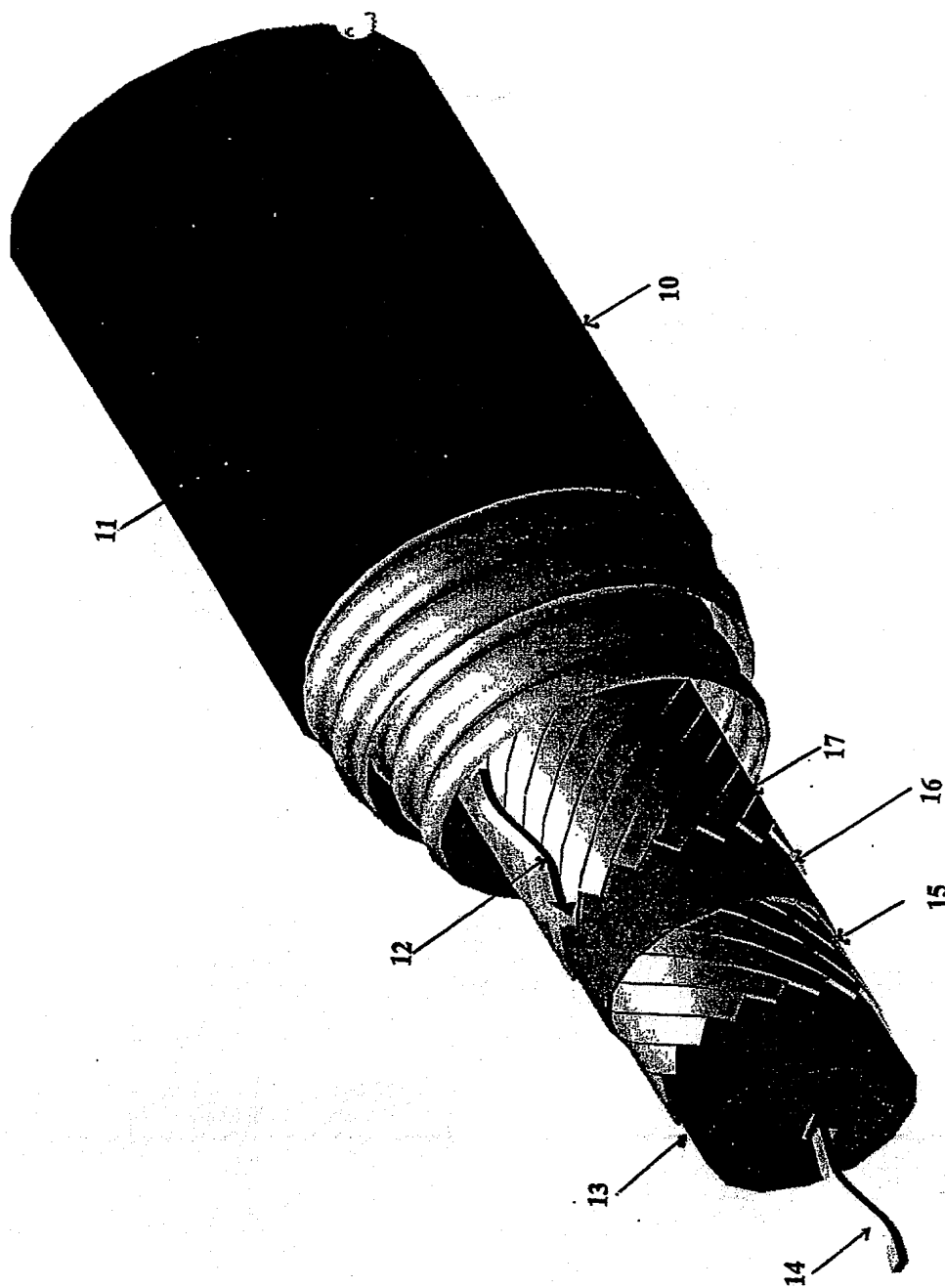


FIGURE 1

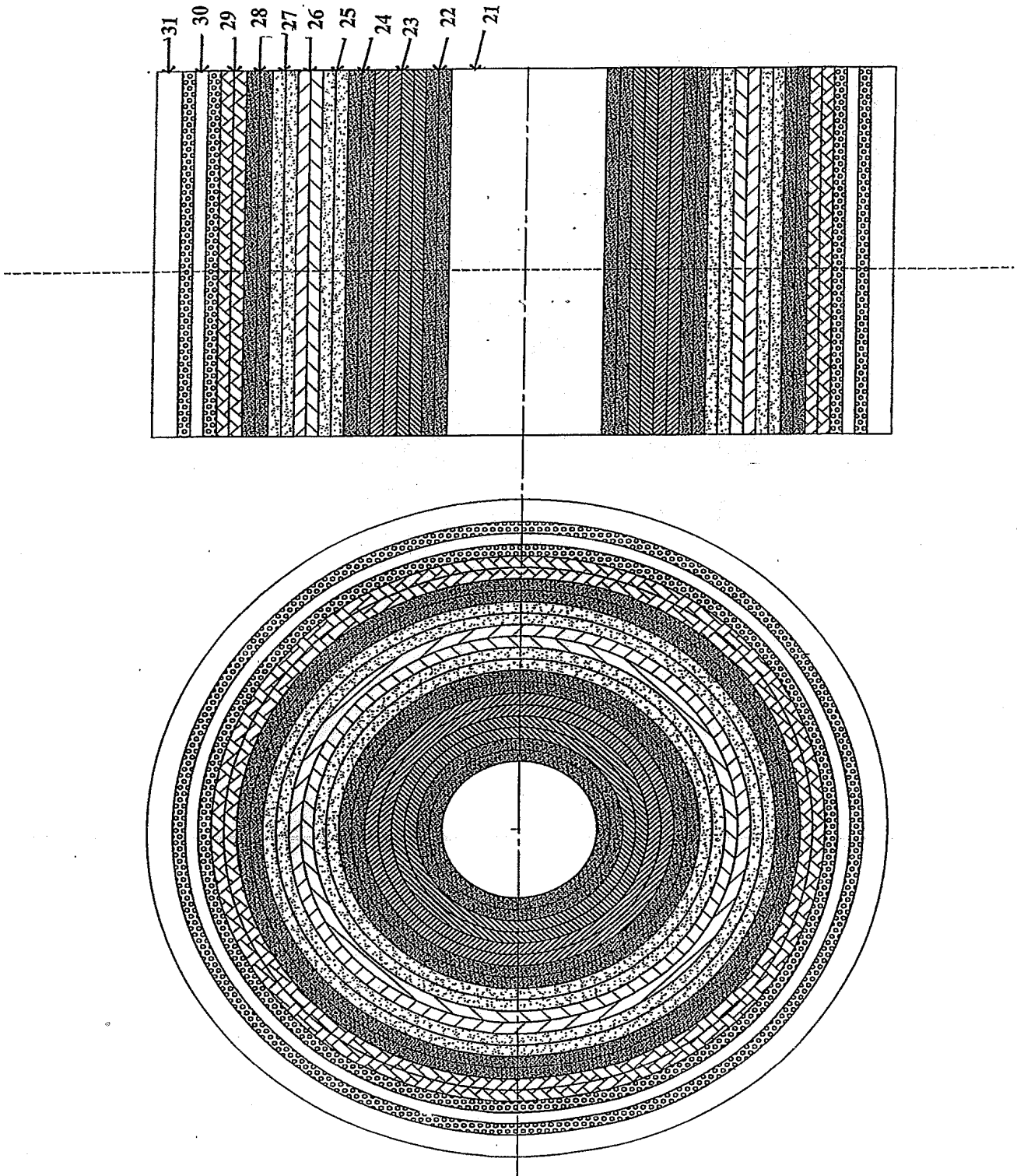


FIGURE 2



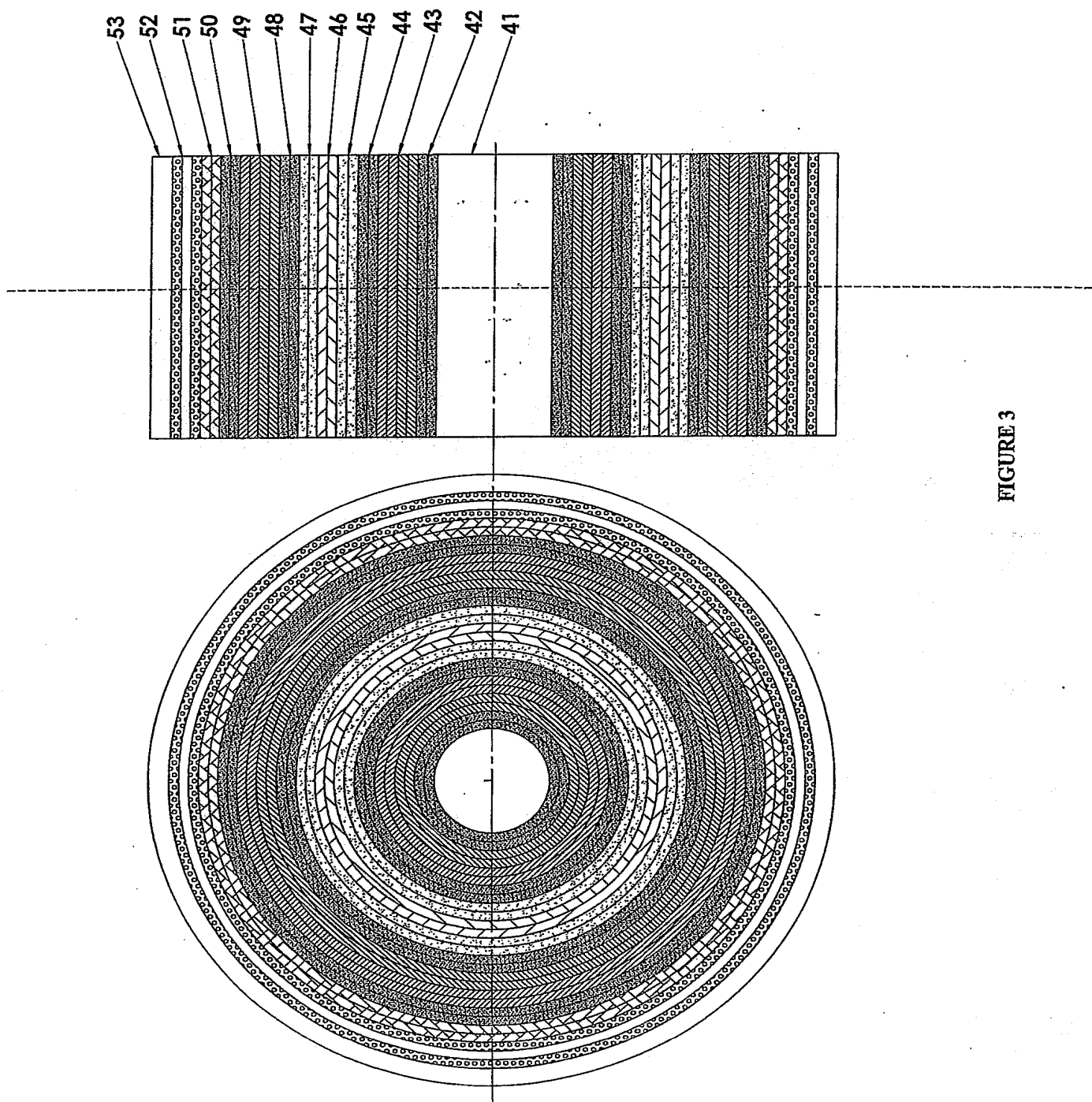


FIGURE 3

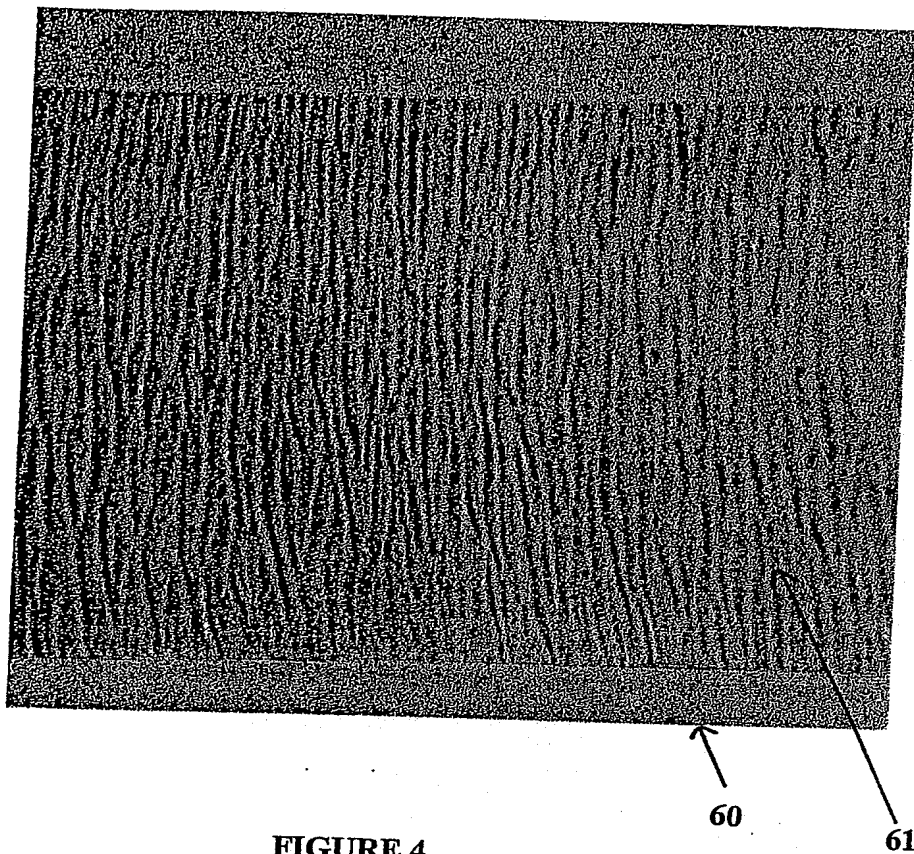


FIGURE 4

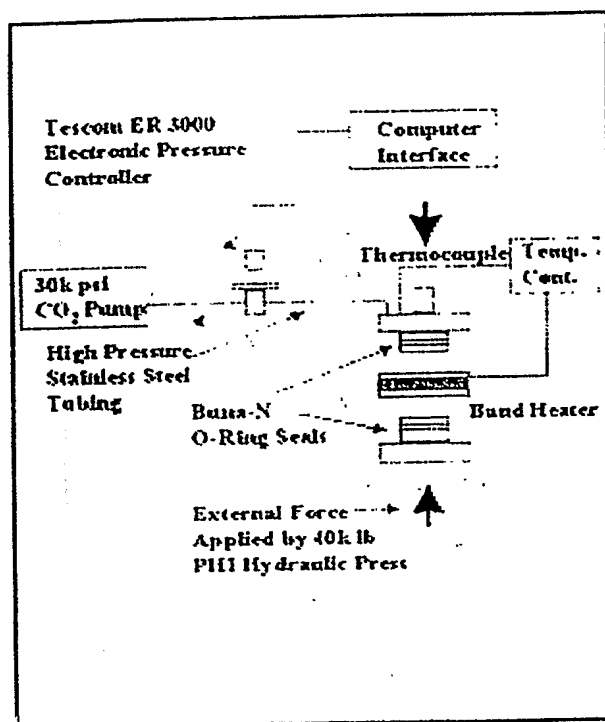
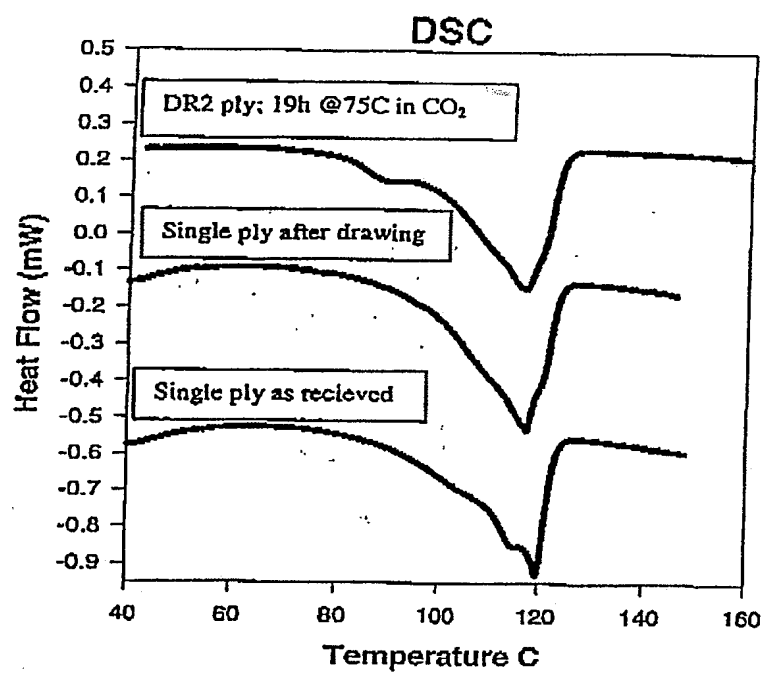
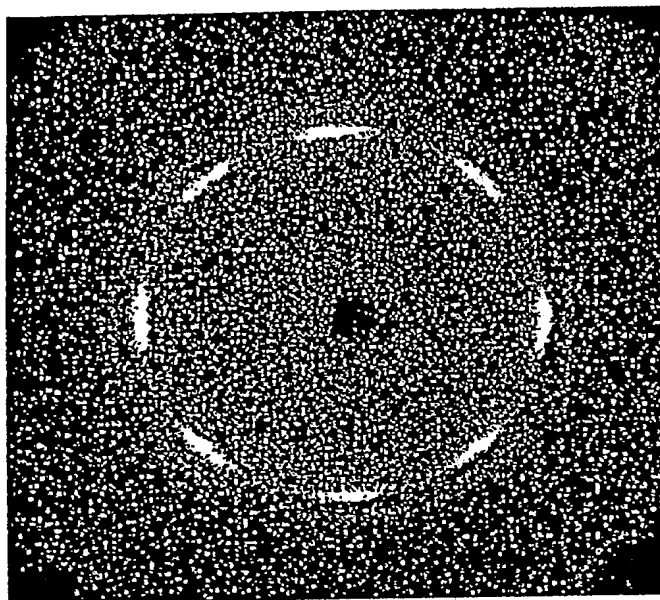


FIGURE 5

**FIGURE 6**



**FIGURE 7**

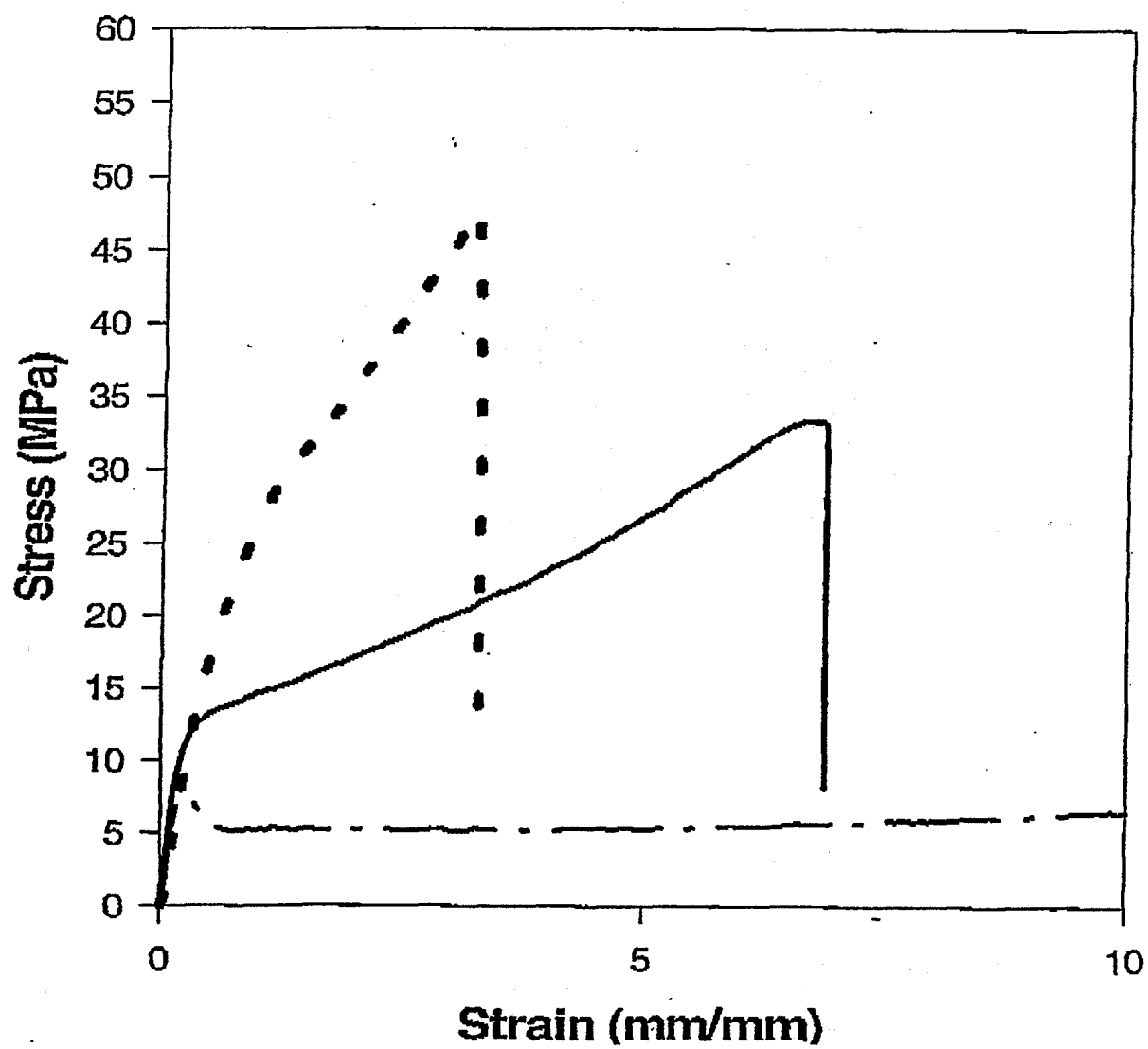


FIGURE 8a

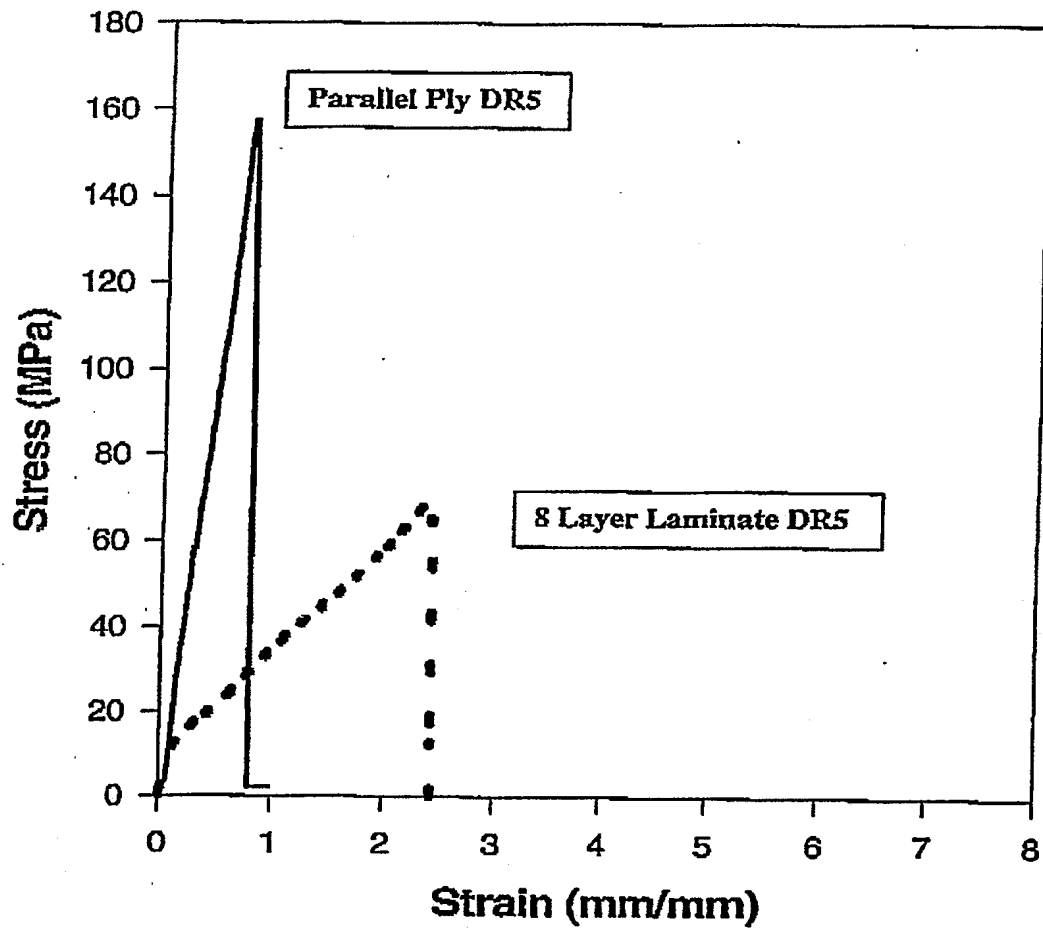


FIGURE 8b

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/28929

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : H01B 12/00

US CL : 174/125.1

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 174/125.1, 505/230, 231, 232, 704

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category *                | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No.   |
|---------------------------|--|---|
| X<br>---<br>Y<br>---<br>A | US 5952614 A (RIES) 14 SEPTEMBER 1999 (14.09.1999), FIG. 4                         | 1, 4-5<br>-----<br>11, 14<br>-----<br>2-3, 6-10, 12-13, 15-67 |
| Y<br>---<br>A             | US 5932523 A (FUJIKAMI et al.) 03 AUGUST 1999 (03.08.1999), FIGS. 3-7              | 11, 14<br>-----<br>1-10, 12-13, 15-67                         |
| A                         | US 3612742 A (SNOWDEN et al.) 12 OCTOBER 1971 (12.10.1971), FIGS. 1-5              | 1-67  |

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

|  |   |     |  |
|--|---|-----|--|
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| "A"                                      | document defining the general state of the art which is not considered to be of particular relevance  | "X" | document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone   |
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| "O"                                      | document referring to an oral disclosure, use, exhibition or other means  |     |  |
| "P"                                      | document published prior to the international filing date but later than the priority date claimed  |     |  |

Date of the actual completion of the international search

16 December 2001 (16.12.2001)

Date of mailing of the international search report

03 JAN 2002

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